

Group Theory in Quantum Mechanics

Lecture 29 (4.30.15)

Based on AMOP Lecture 18-19

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

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

OUTLINE

	<u>Example(s)</u>
<i>Introductory review</i>	
• <i>Rovibronic nomograms and PQR structure</i>	v_3 and v_4 SF_6
• <i>Rotational Energy Surfaces (RES) and θ'_K-cones</i>	v_4 P(88) SF_6
• <i>Spin symmetry correlation tunneling and entanglement</i>	SF_6
<i>Recent developments</i>	
• <i>Analogy between PE surface and RES dynamics</i>	
• <i>Rotational Energy Eigenvalue Surfaces (REES)</i>	v_3 SF_6

Review: SF_6 levels and nomograms for Coriolis PQR structure

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

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

$$\begin{aligned} H^{\text{Scalar Coriolis}} &= -B\zeta \mathbf{2J}^{\text{Total}} \cdot \ell^{\text{vibe}} \\ &= -B\zeta [\mathbf{J}^2 - (\mathbf{J}-\ell)^2 + \ell^2] \\ &= -B\zeta [\mathbf{J}^2 - \mathbf{N}^2 + \ell^2] \\ &= -B\zeta [J(J+1) - N(N+1) + \ell(\ell+1)] \end{aligned}$$

Involves:

angular momentum ℓ of vibration "orbits"

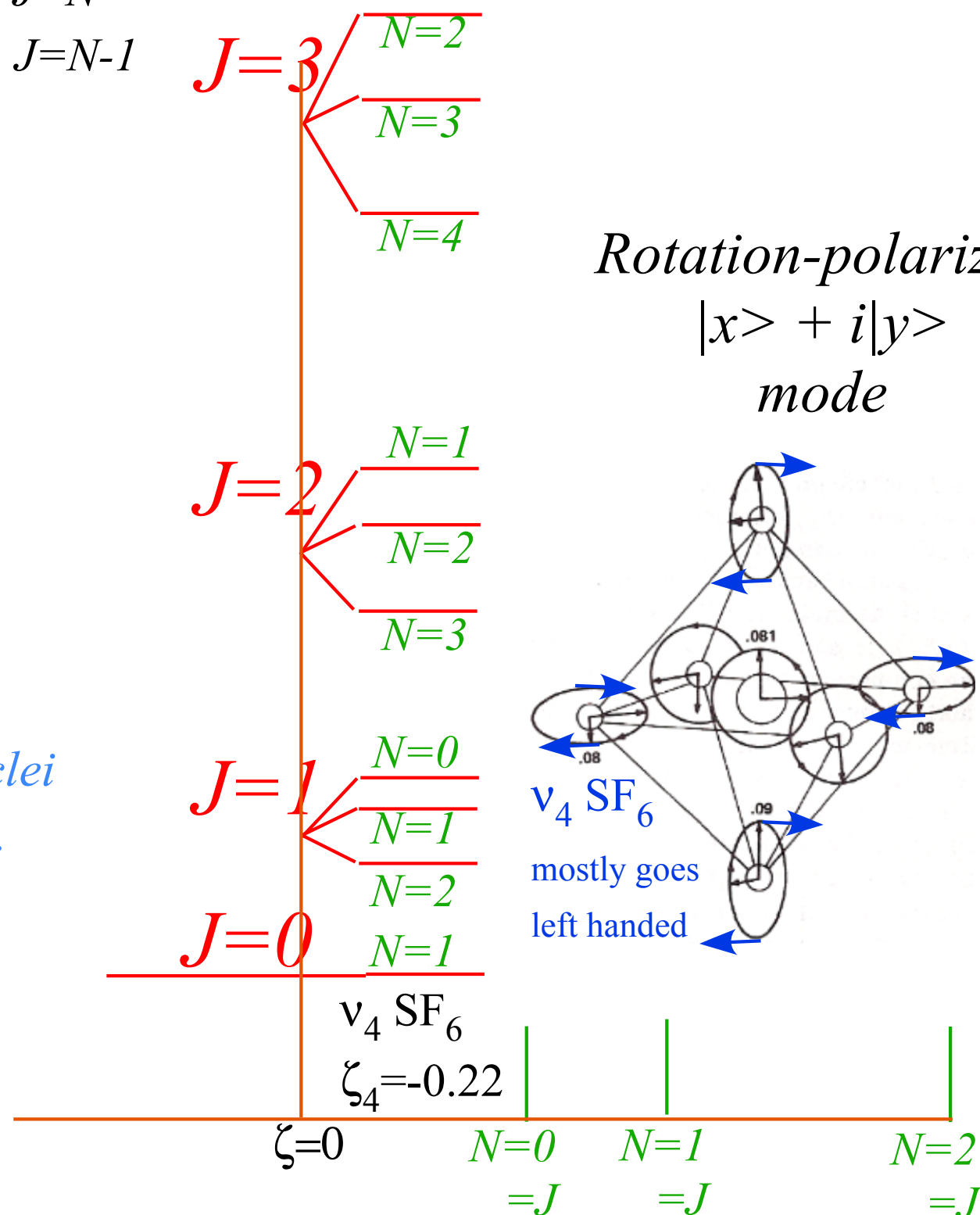
angular momentum \mathbf{N} (or \mathbf{R}) of rotating nuclei

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

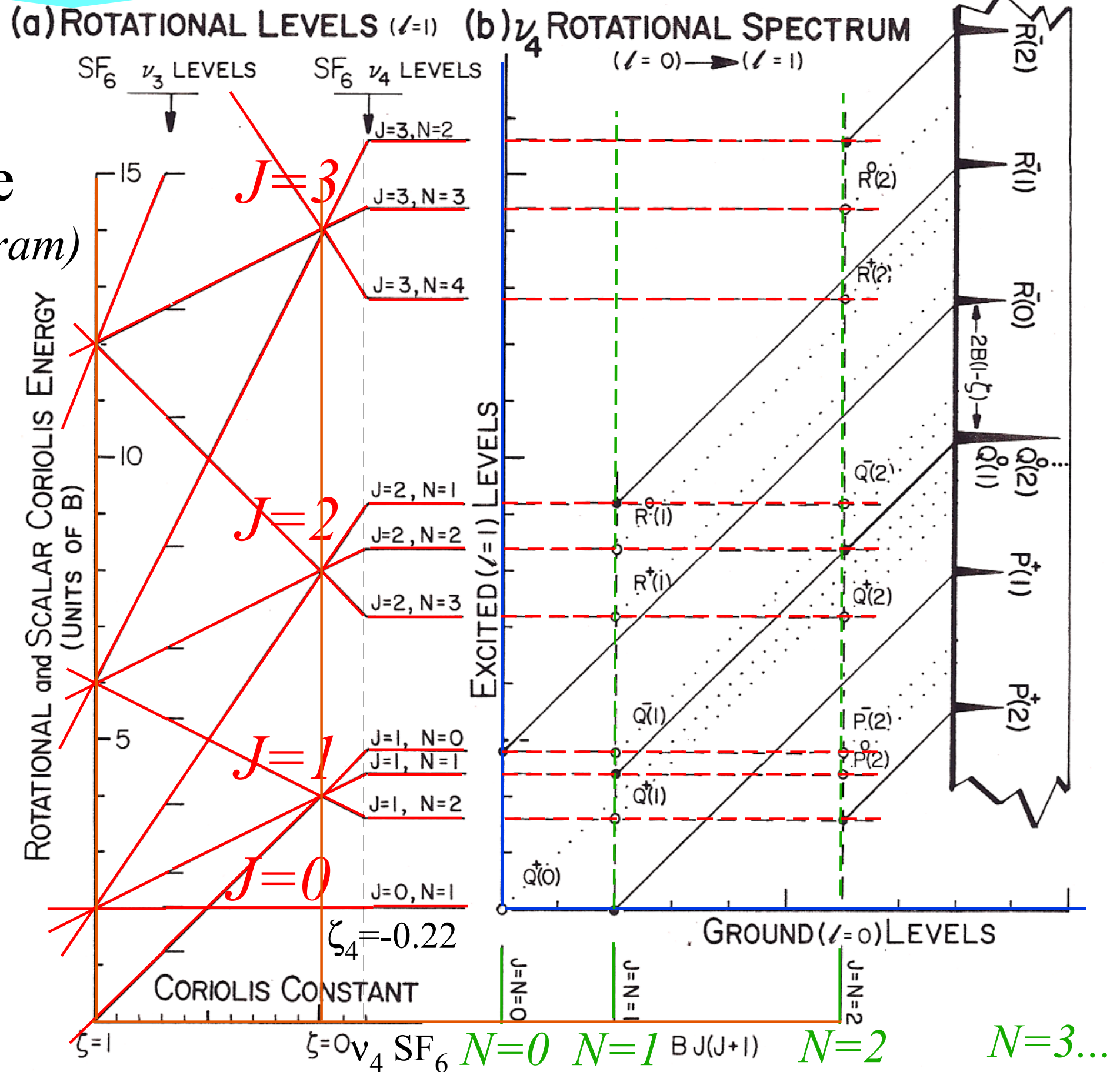
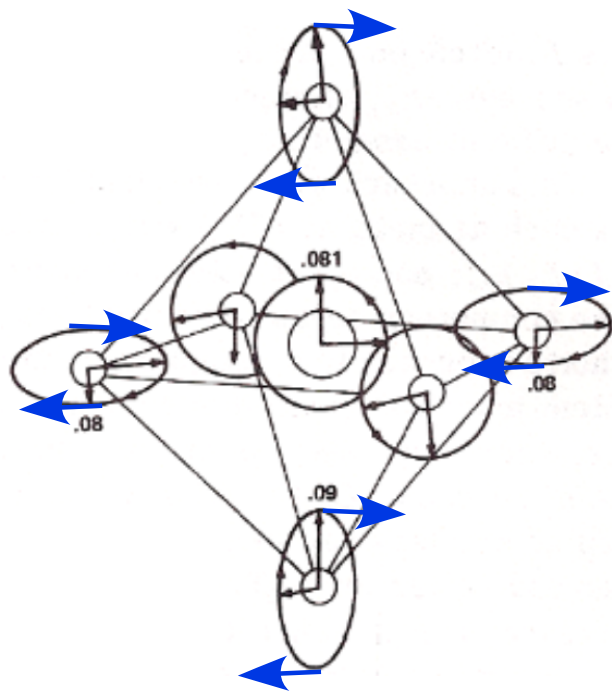
$\langle 2\mathbf{J} \cdot \ell \rangle = J(J+1) - N(N+1) + \ell(\ell+1)$



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

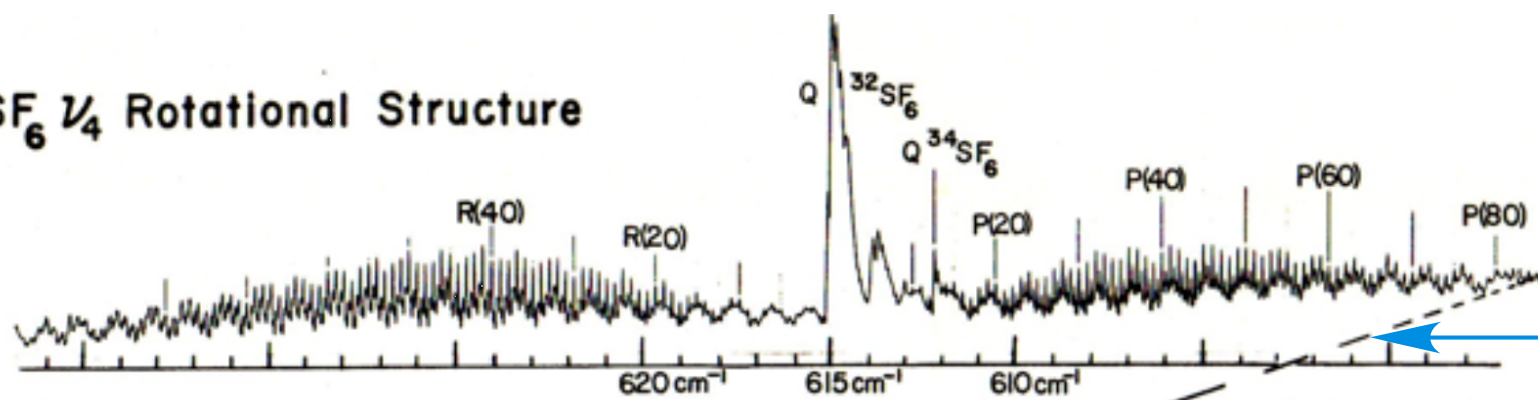
Summary of low-J (PQR) ro-vibe structure

(Using ro-vib. nomogram)



Review: SF_6 levels and nomograms for Coriolis PQR structure

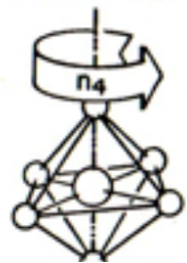
(a) SF_6 ν_4 Rotational Structure



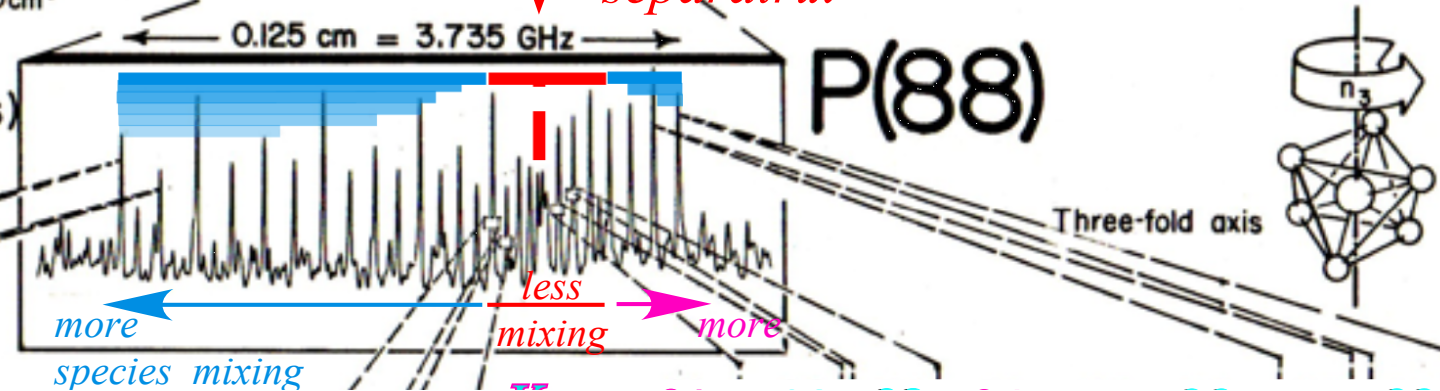
FT IR and Laser Diode Spectra
K.C. Kim, W. B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. **76**, 322 (1979).

Primary AET species mixing increases with distance from "separatrix"

(b) P(88) Fine Structure (Rotational anisotropy effects)



Four fold axis



Three-fold axis

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

$$\langle H \rangle \sim v_{\text{vib}} + B J(J+1) + \langle H^{\text{Scalar Coriolis}} \rangle + \langle H^{\text{Tensor Centrifugal}} \rangle + \langle H^{\text{Nuclear Spin}} \rangle + \langle H^{\text{Tensor Coriolis}} \rangle + \dots$$

OUTLINE

Introductory review

- | | <u>Example(s)</u> |
|---|------------------------|
| • <i>Rovibronic nomograms and PQR structure</i> | v_3 and v_4 SF_6 |
| • <i>Rotational Energy Surfaces (RES) and θ'_K-cones</i> | v_4 P(88) SF_6 |
| • <i>Spin symmetry correlation tunneling and entanglement</i> | SF_6 |
| <i>Recent developments</i> | |
| • <i>Analogy between PE surface and RES dynamics</i> | |
| • <i>Rotational Energy Eigenvalue Surfaces (REES)</i> | v_3 SF_6 |

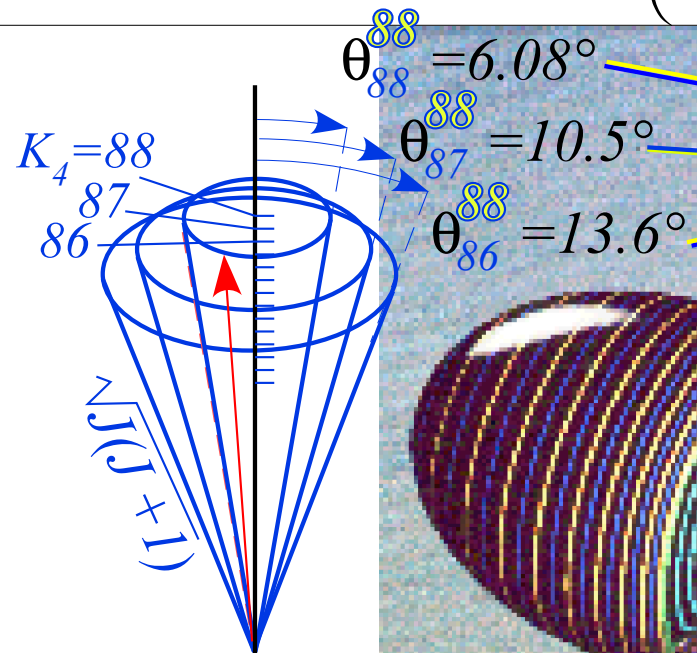
Review: SF_6 spectral clusters of symmetry species $O \supset C_4$ and $O \supset C_3$ symmetry correlation

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

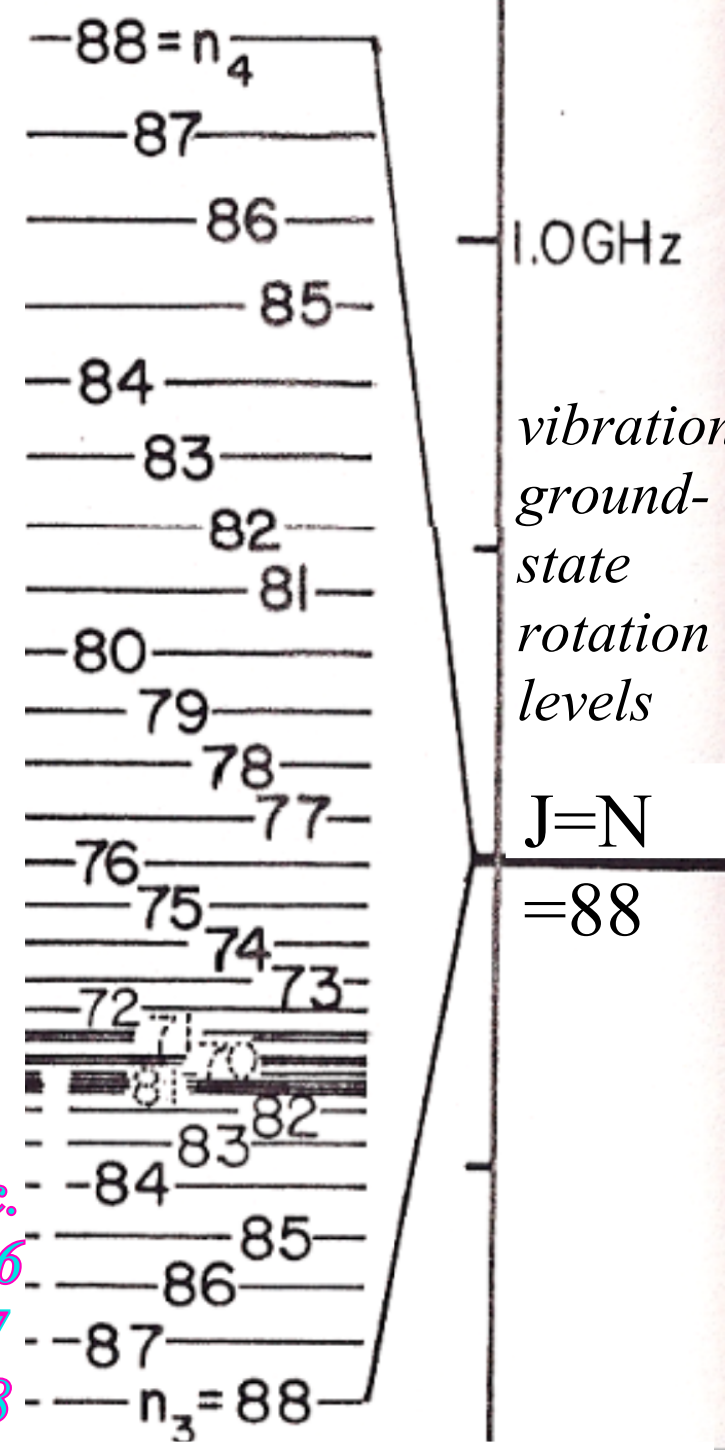
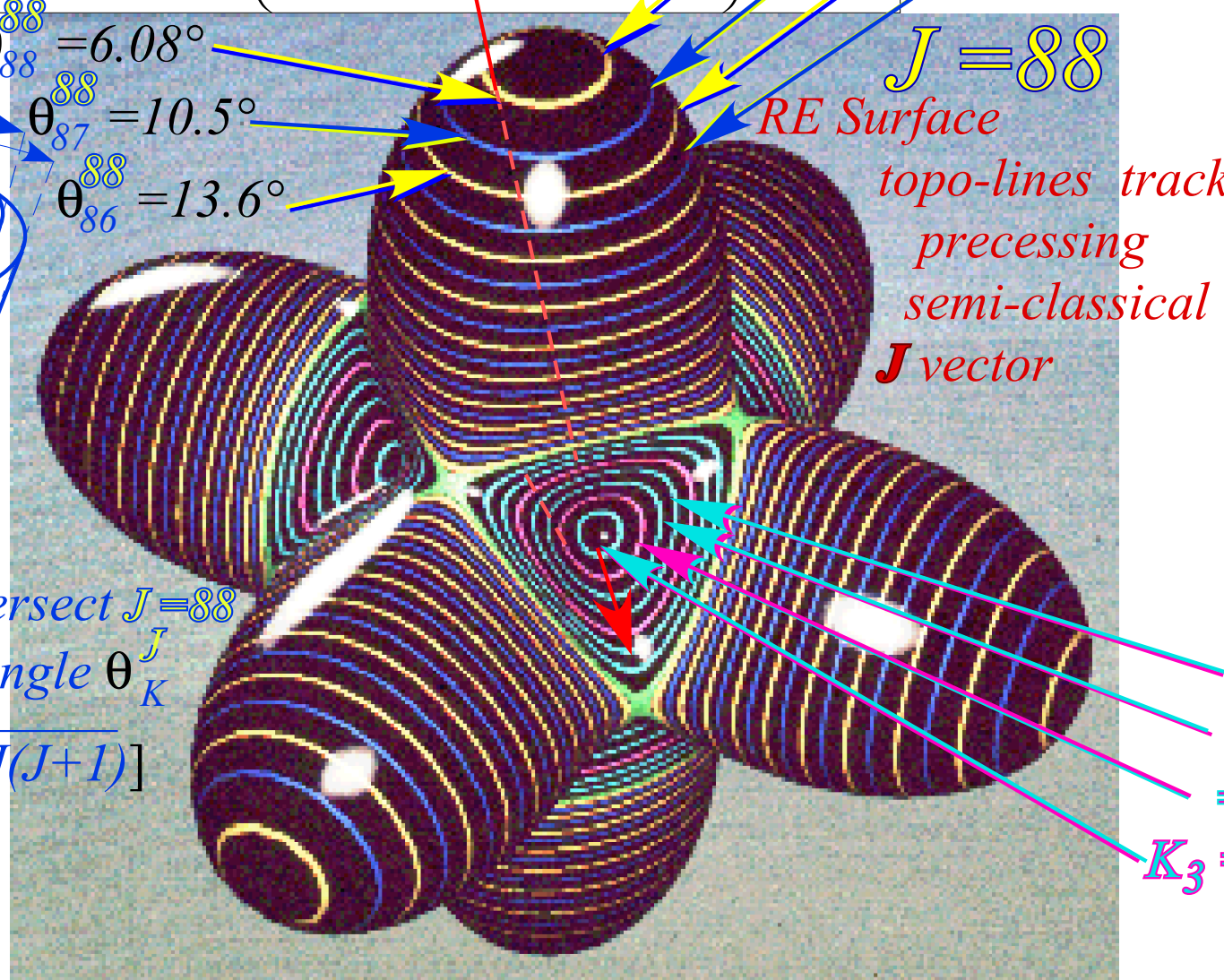
O_h or T_d Spherical Top: (Hecht CH_4 Hamiltonian 1960)

$$H = B \left(J_x^2 + J_y^2 + J_z^2 \right) + t_{440} \left(J_x^4 + J_y^4 + J_z^4 - \frac{3}{5} J^4 \right) + \dots$$

$$= BJ^2 + t_{440} \left(T_0^4 + \sqrt{\frac{5}{14}} [T_4^4 + T_{-4}^4] \right) + \dots$$



(J,K) cones intersect $J=88$ RE surface at angle θ_K^J
 $\theta_K^J = \arccos[K/\sqrt{J(J+1)}]$

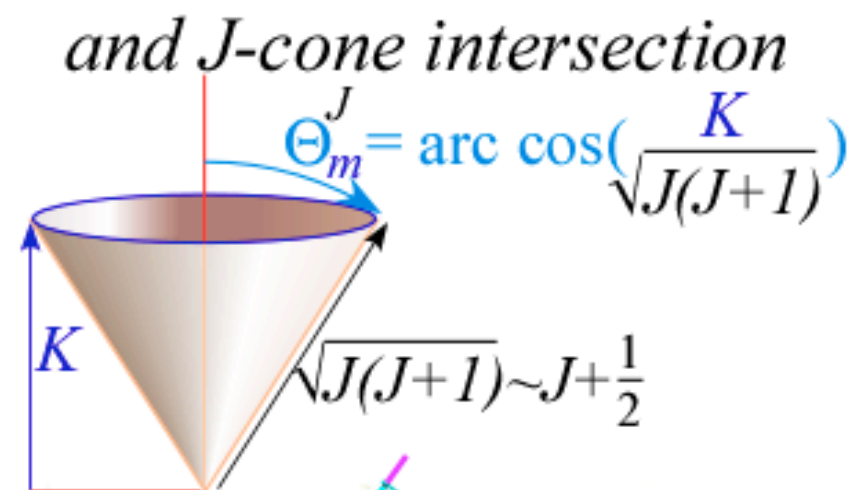


etc.
 =86
 =87
 $K_3=88$

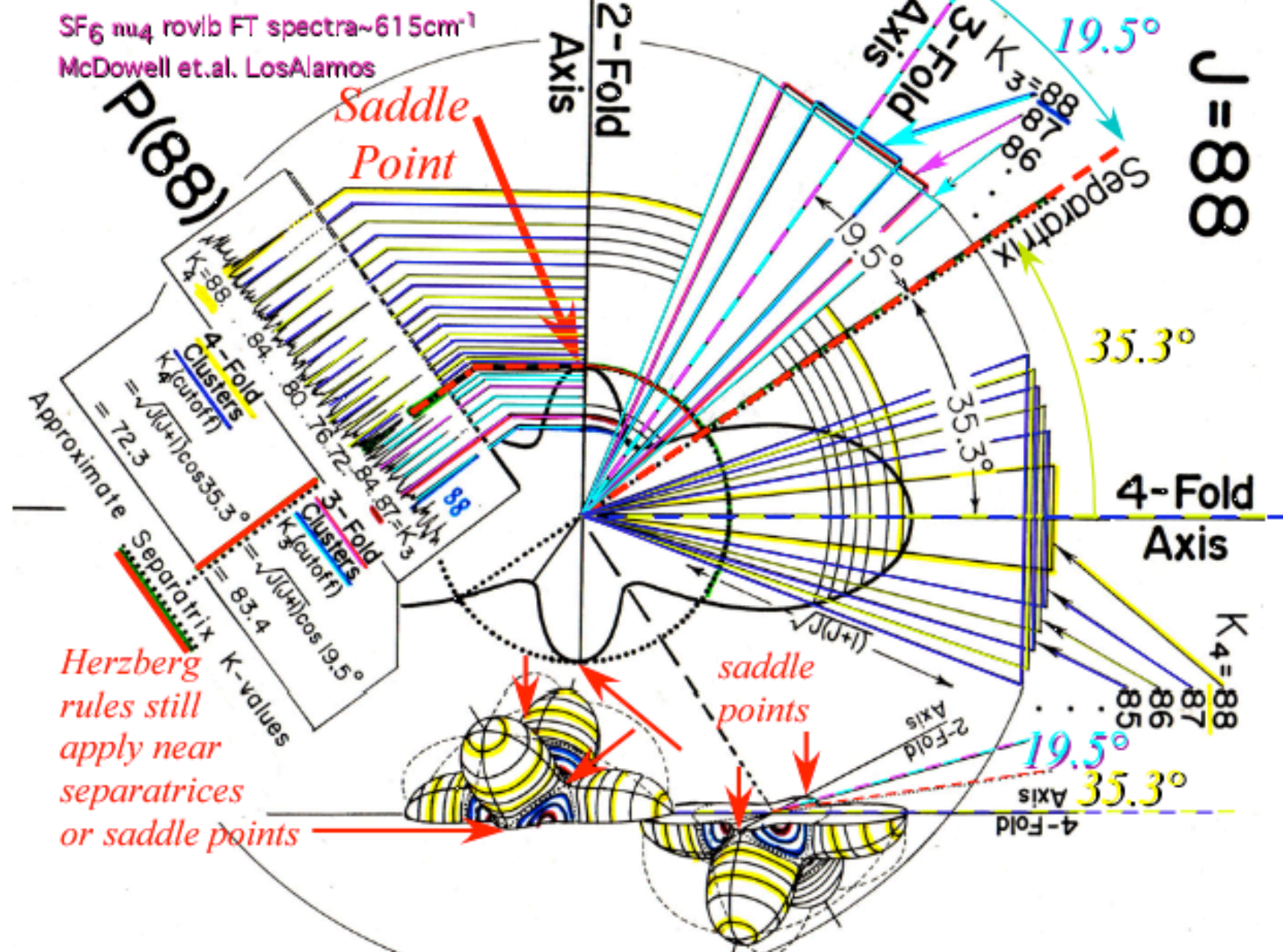
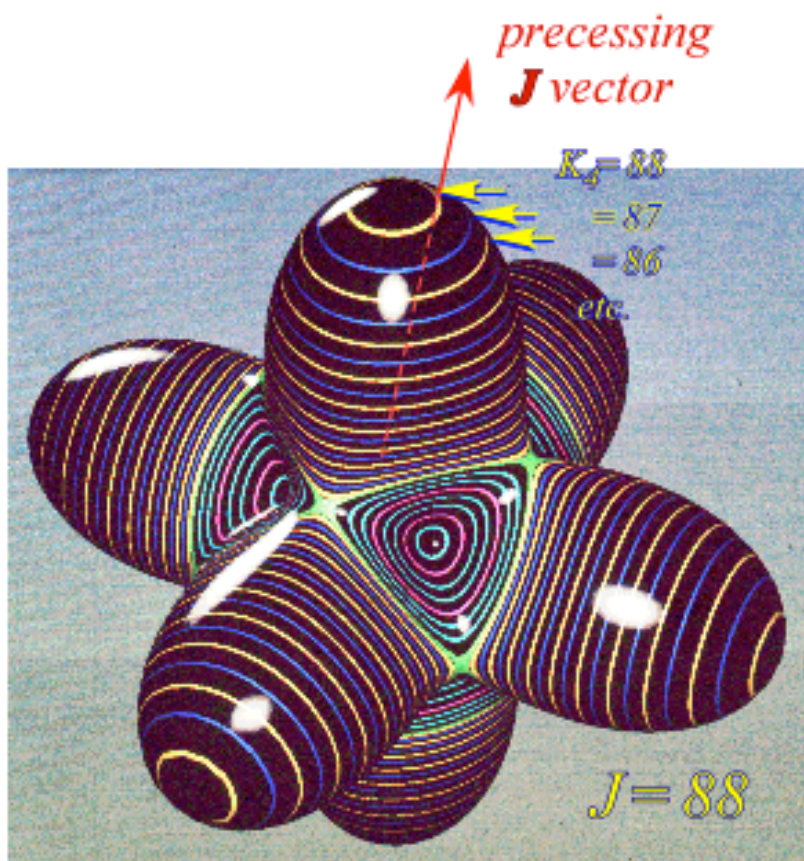
SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography and J-cone intersection

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

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

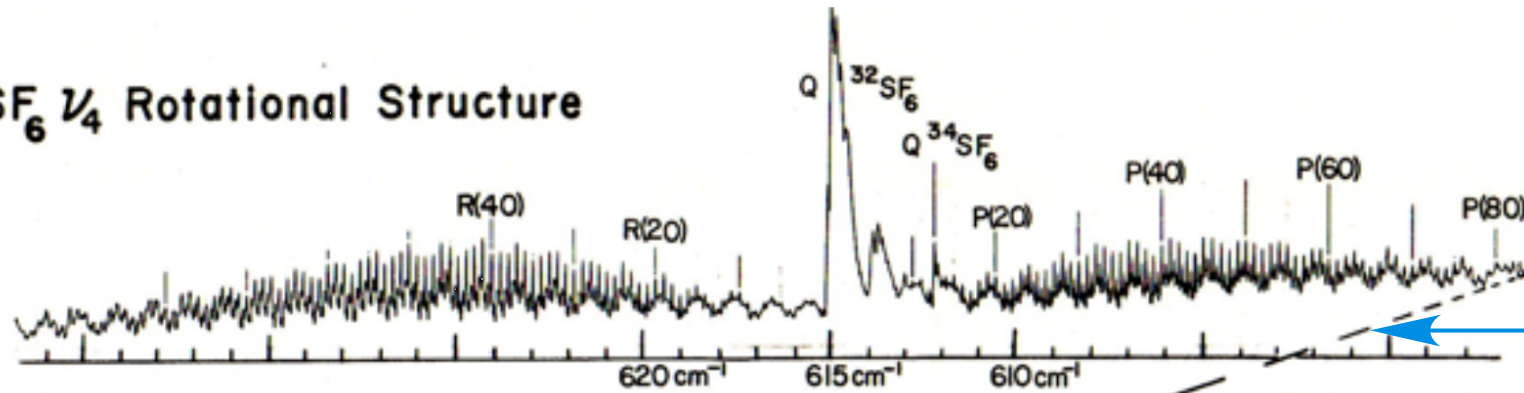


Rovibronic Energy (RE) Tensor Surface



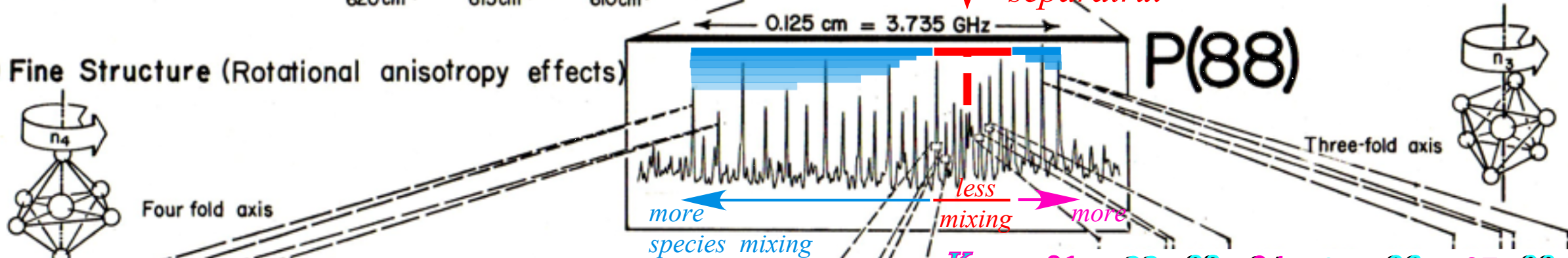
Review: SF_6 spectral clusters of symmetry species $O \supset C_4$ and $O \supset C_3$ symmetry correlation

(a) $SF_6 \nu_4$ Rotational Structure

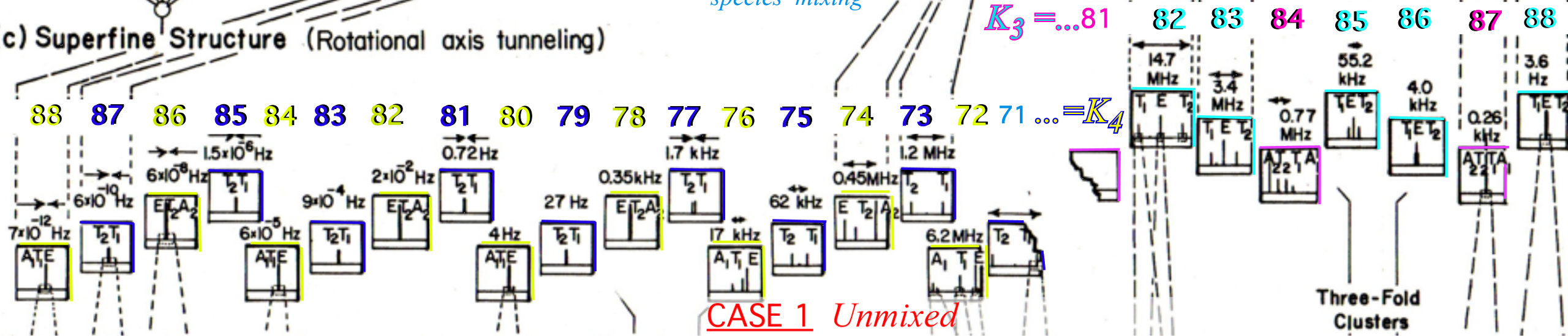


Primary AET species mixing increases with distance from "separatrix"

(b) P(88) Fine Structure (Rotational anisotropy effects)



(c) Superfine Structure (Rotational axis tunneling)



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

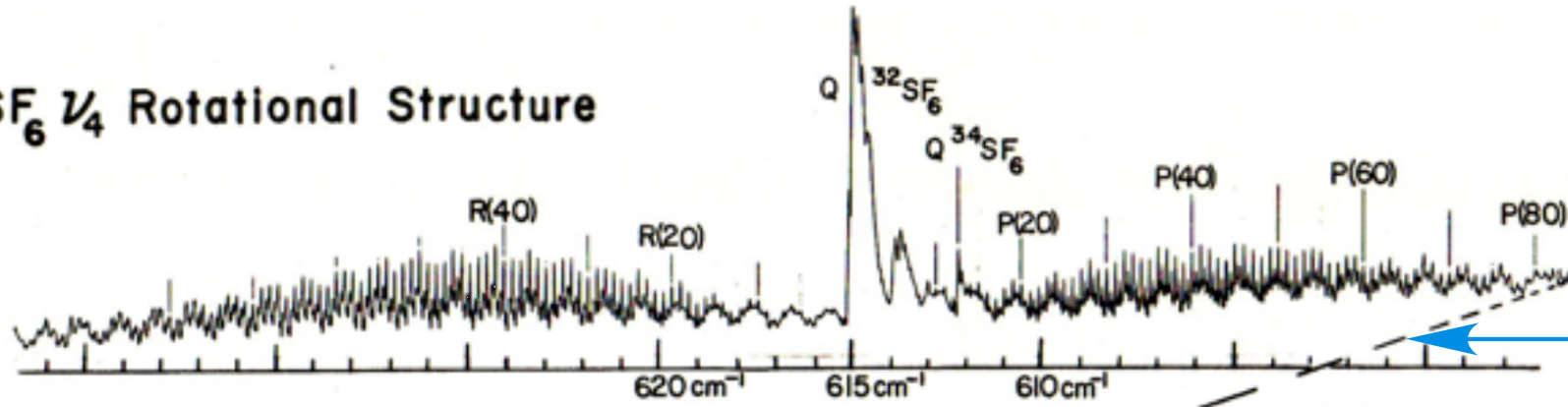
$P(N) = P(88)$ structure due to tensor centrifugal/Coriolis due to vibrational ℓ and total momentum $\mathbf{J} = \ell + \mathbf{N}$

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

Review: SF_6 spectral clusters of symmetry species $O \supset C_4$ and $O \supset C_3$ symmetry correlation

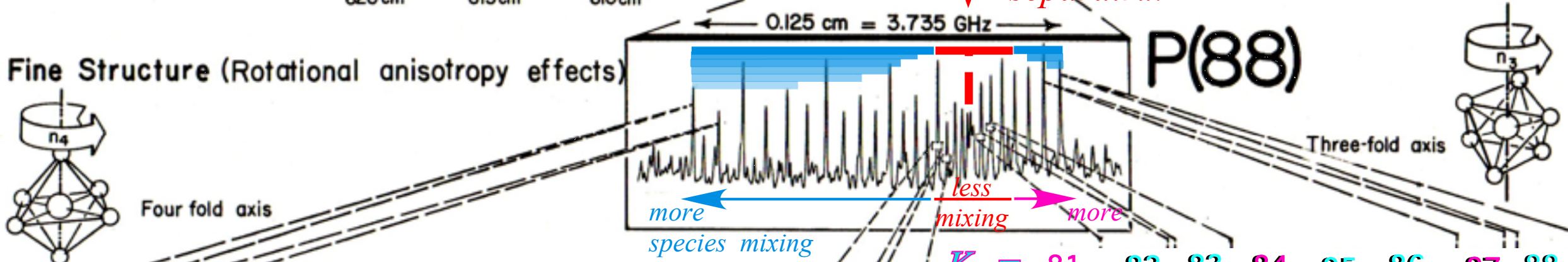
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).

(a) $SF_6 \nu_4$ Rotational Structure



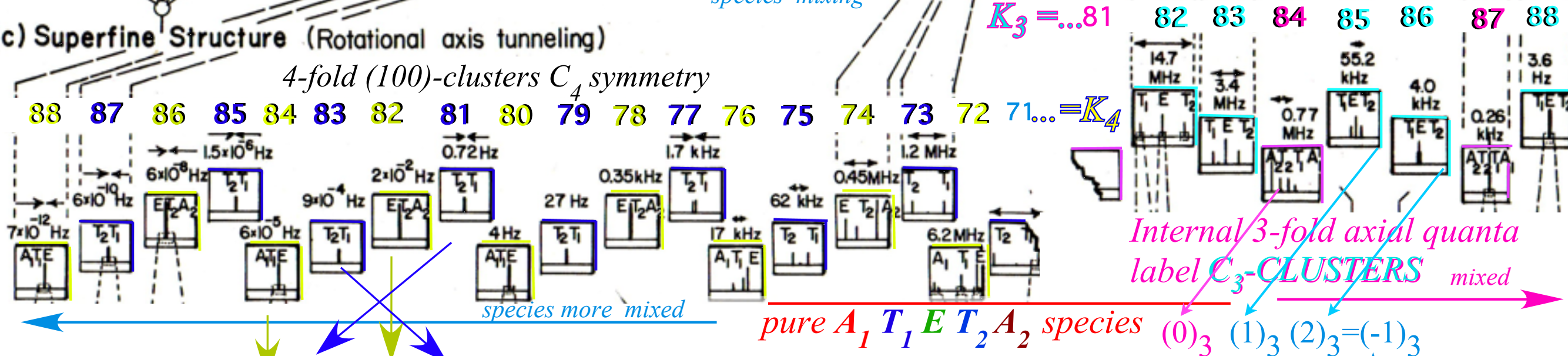
Primary AET species mixing increases with distance from "separatrix"

(b) P(88) Fine Structure (Rotational anisotropy effects)



(c) Superfine Structure (Rotational axis tunneling)

4-fold (100)-clusters C_4 symmetry



Cubic Octahedral symmetry O

A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

$(0)_4 (1)_4 (2)_4 (3)_4 = (-1)_4$
3 modulo 4 equals -1 modulo 4 (and 83 mod 4)
 $83 = 84 - 1$

4-fold (100) C_4 symmetry clusters
3-fold (111) C_3 symmetry clusters

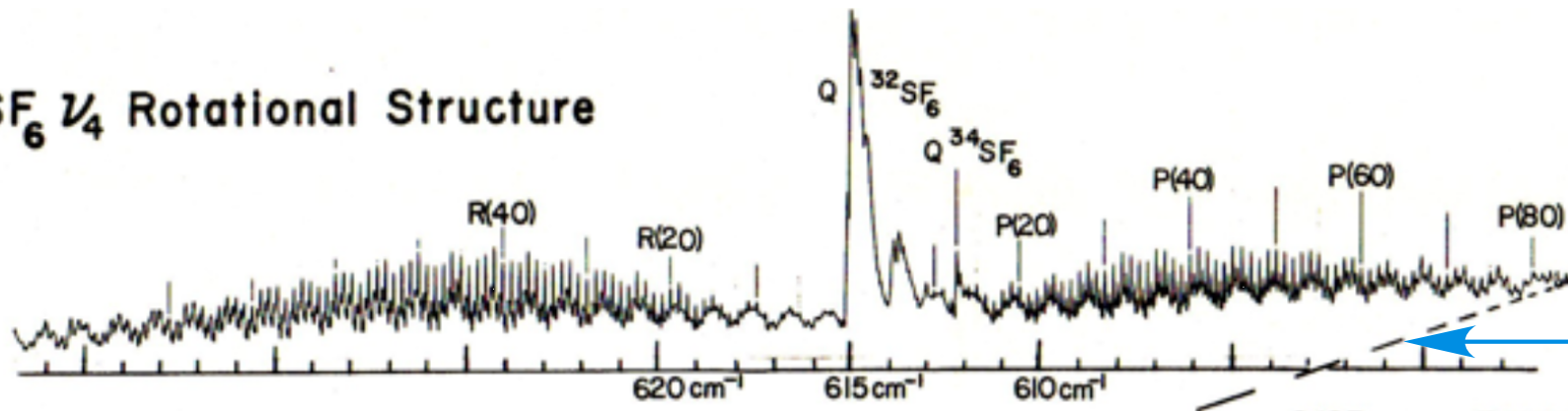
A_1	1	•	•
A_2	1	•	•
E	•	1	1
T_1	1	1	1
T_2	1	1	1

$(0)_3 (1)_3 (2)_3 = (-1)_3$
(2 modulo 3 equals -1 modulo 3 and 86 mod 3)
 $86 = 88 - 1$

Review: SF_6 spectral clusters of symmetry species $O \supset C_4$ and $O \supset C_3$ symmetry correlation

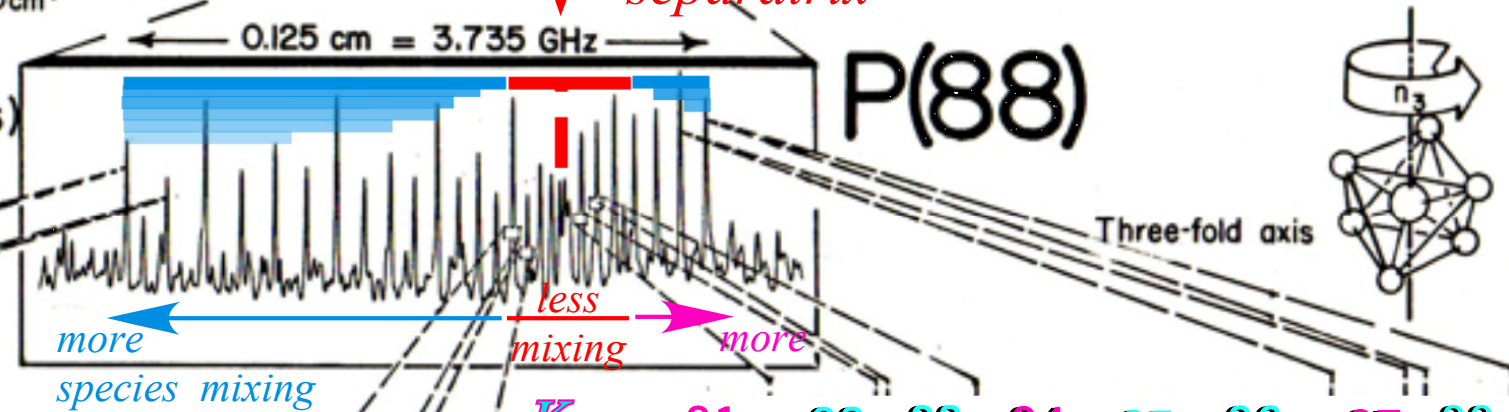
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).

(a) SF_6 ν_4 Rotational Structure

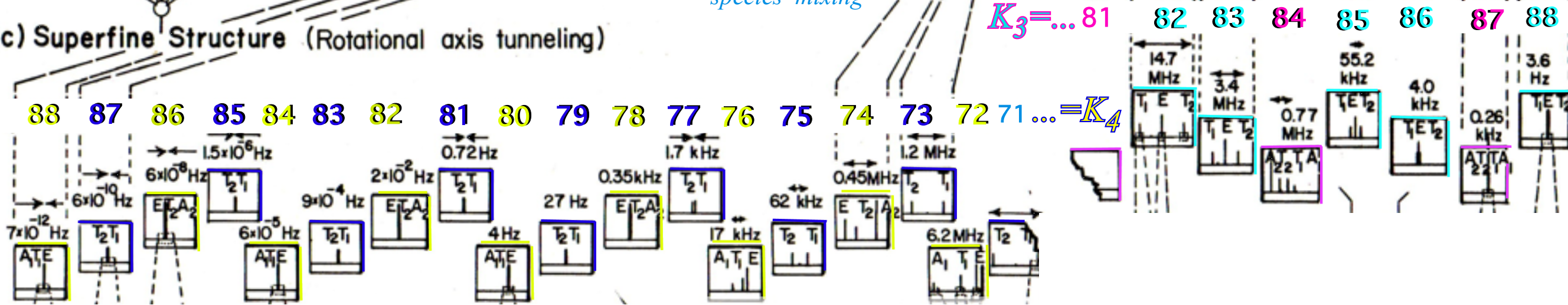


Primary AET species mixing increases with distance from "separatrix"

(b) P(88) Fine Structure (Rotational anisotropy effects)

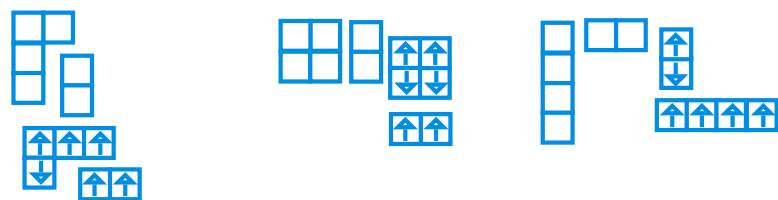


(c) Superfine Structure (Rotational axis tunneling)



CASE 2₄

Broken 4 + 2 tableau state description

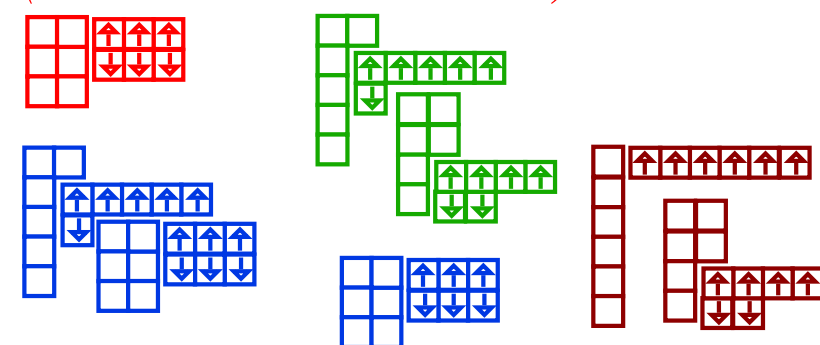


Spin-rovib ENTANGLEMENT symmetry

CASE 1 Unmixed

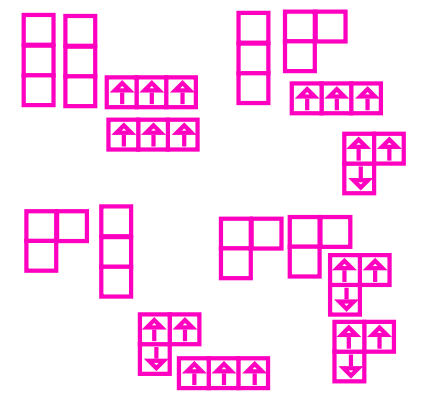
primary $A_1 T_1 E T_2 A_2$ species

(Whole 6-box tableaux)



CASE 2₃

Broken 3 + 3 Tableaus



 *Conservation (or not!) of rovibronic spin-symmetry-species*
Entanglement and related issues

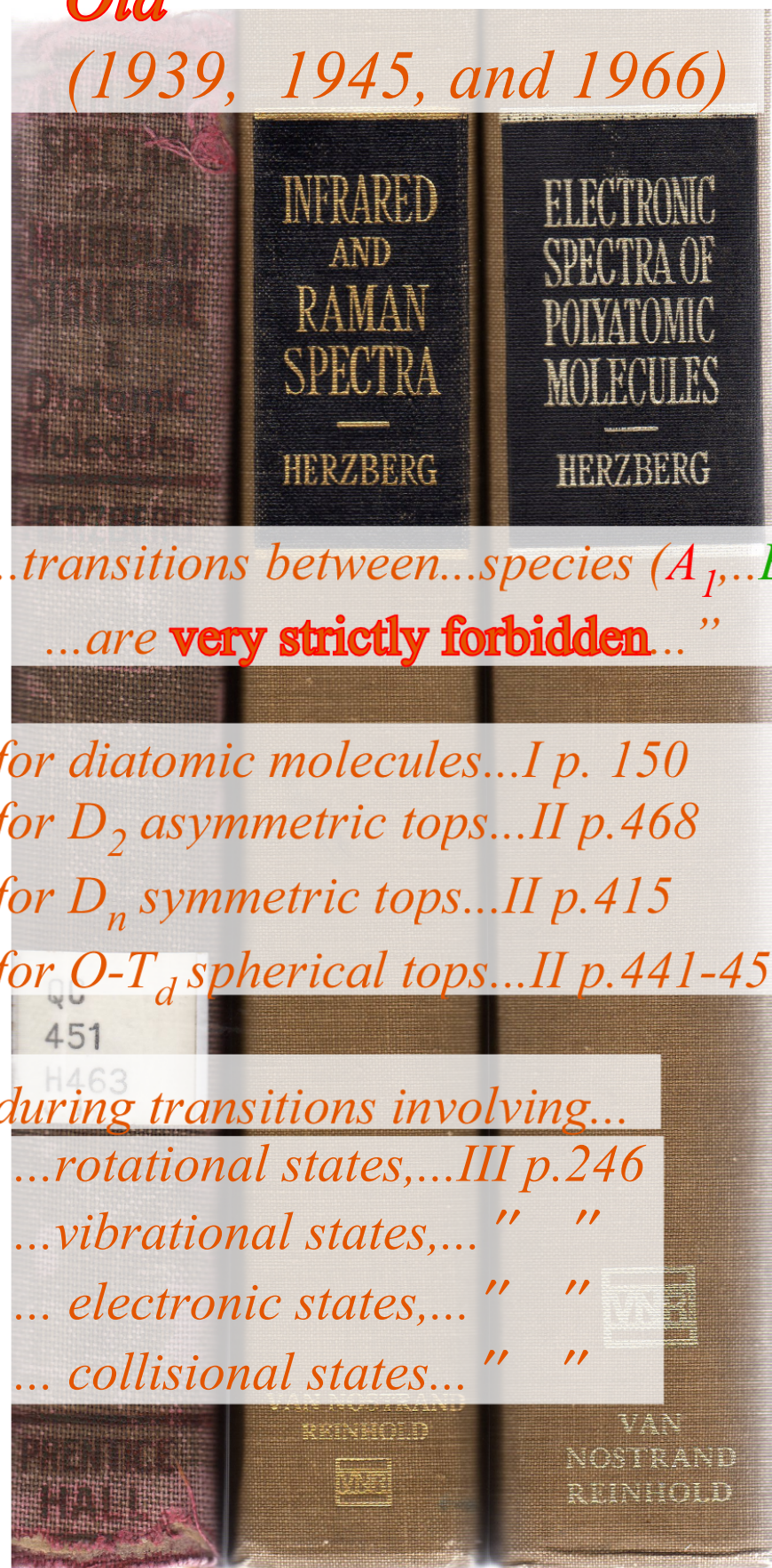
CONSERVATION OF ROVIBRONIC SPIN-SPECIES - Two Views:

Old

(1939, 1945, and 1966)

versus

New (1978- 2005)



“...transitions between...species ($A_1, \dots E, \dots T_2 \dots$)
...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... " "

www.sciencemag.org SCIENCE VOL 310 23 DECEMBER 2005
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 months.

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

Strictly versus

NOT!

Conservation and preservation?

No Way! versus

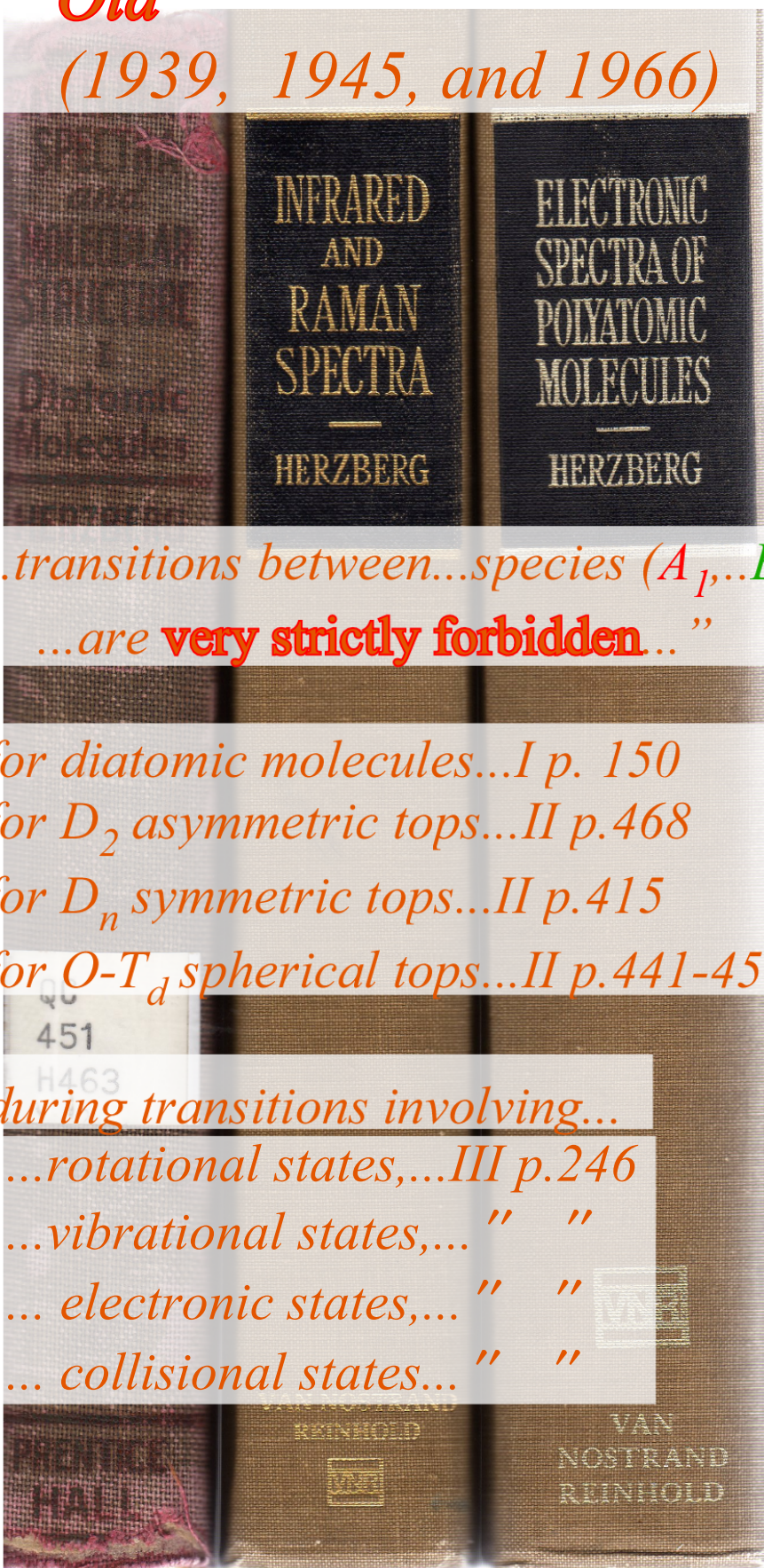
WAY!

Conversion, perversion or transition?

CONSERVATION OF ROVIBRONIC SPIN-SPECIES - Two Views:

Old

(1939, 1945, and 1966)



“...transitions between...species ($A_1, \dots E, \dots T_2, \dots$)
...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)

www.sciencemag.org SCIENCE VOL 310 23 DECEMBER 2005
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 months.

[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?

To **conserve** vs. To **convert**
To **preserve** vs. To **pervert**

Widespread and extreme mixing of species reported in CF_4 , SiF_4 and SF_6 :
perversion

Ch. Borde, *Phys. Rev. A* 20,254(1978)(expt.)
Harter, *Phys. Rev. A* 24,192 (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*

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

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

No Way!

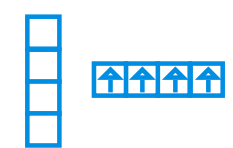
WAY!

and...

What is it?

SPIN SYMMETRY correlation has a new name...

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.)

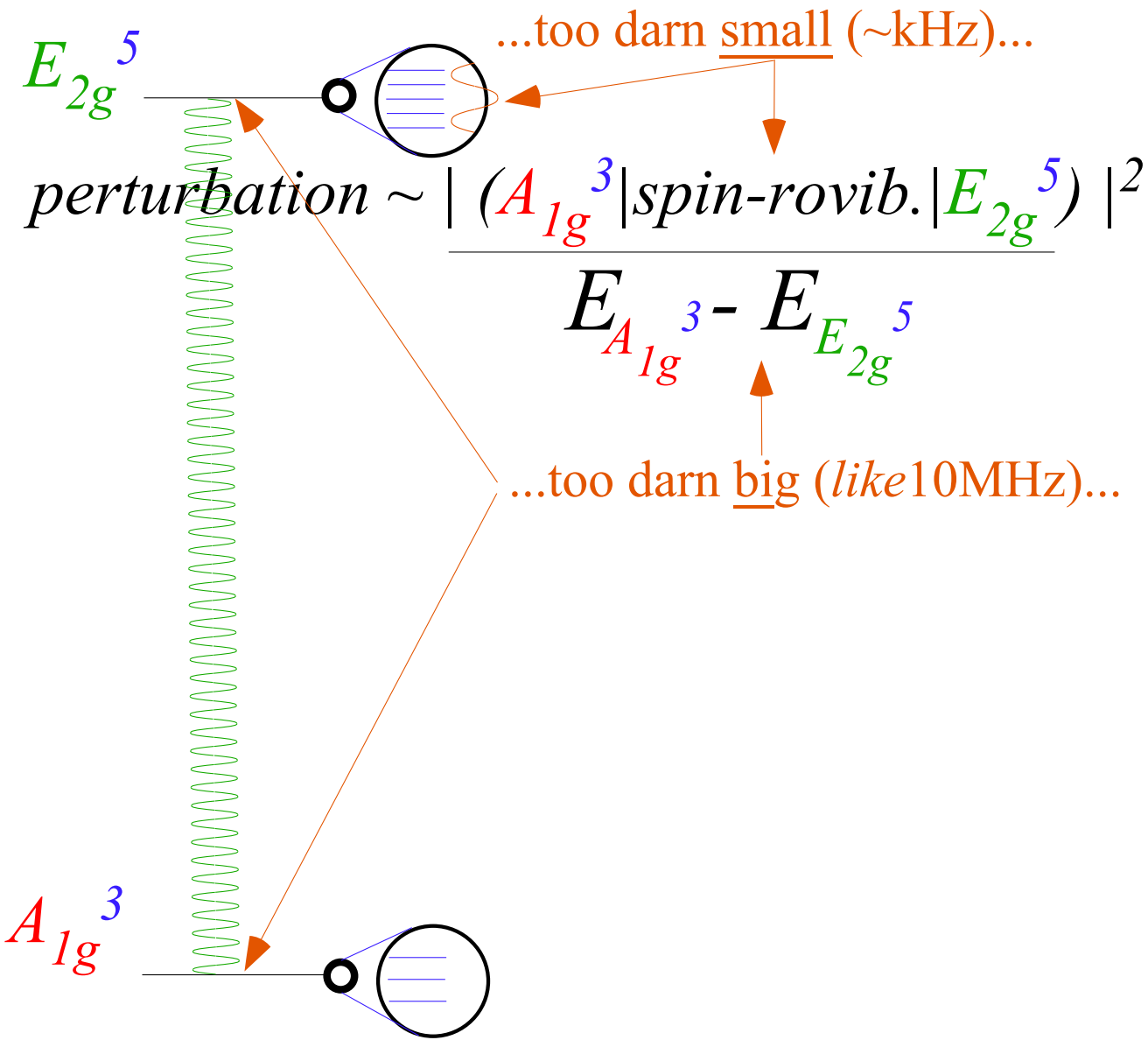
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

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

A_{2u}^1

No Way!

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



HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

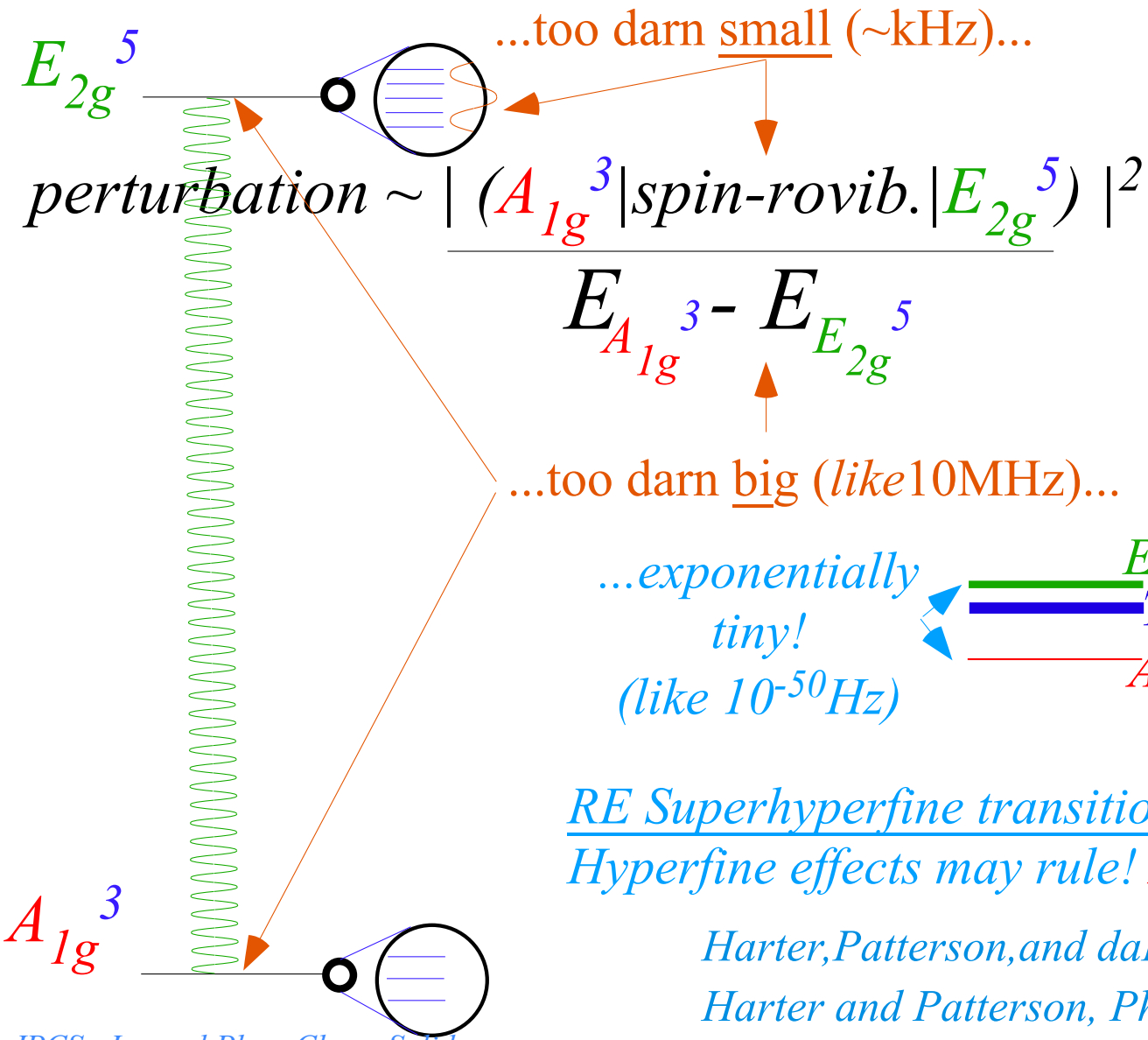
What preserves it? versus *What mixes it up?*

No Way!

WAY!

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

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

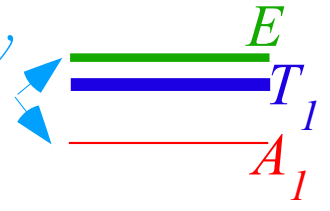


perturbation $\sim \left| \langle A_{1g}^3 | \text{spin-rovib.} | E_{2g}^5 \rangle \right|^2$

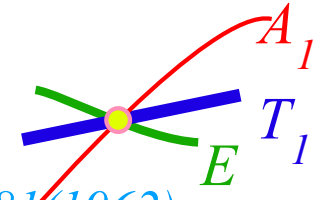
$$\frac{E_{A_{1g}^3} - E_{E_{2g}^5}}$$

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

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



“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) (CF₄)
Harter, Phys. Rev. A24,192-262(1981) (SF₆)

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

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

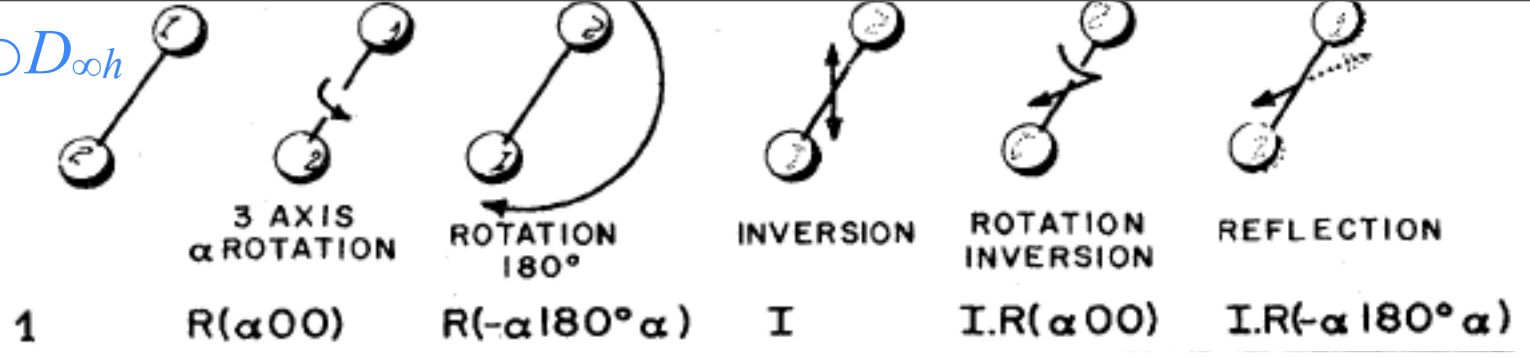
Labeling by symmetry $O(3) \supset D_{\infty h}$

Coriolis and λ -doubling levels

Dipole-allowed transitions

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

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



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

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

- $A_{1g} = \Sigma_g^+$
- $A_{1u} = \Sigma_u^+$
- $A_{2g} = \Sigma_g^-$
- $A_{2u} = \Sigma_u^-$
- $E_{1g} = \pi_g$
- $E_{1u} = \pi_u$
- $E_{2g} = \Delta_g$
- $E_{2u} = \Delta_u$
- \vdots

A, B, or C Correlations

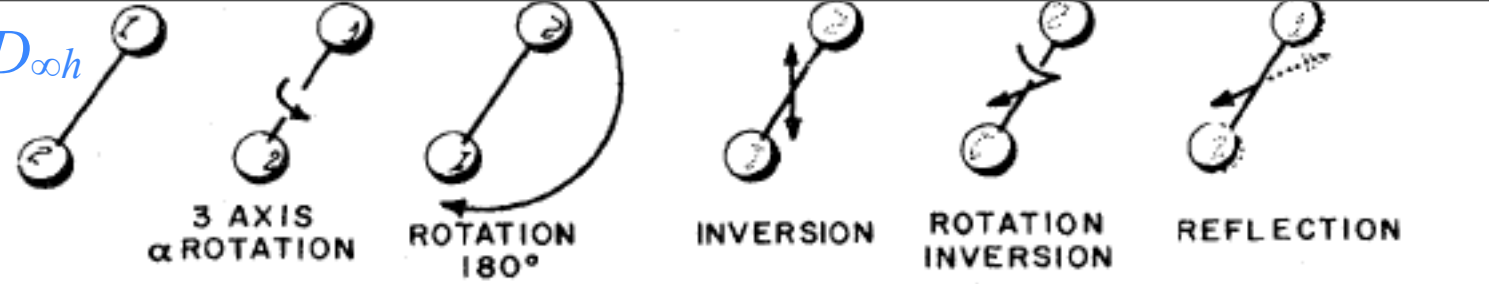
$B =$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	$\Delta_u \dots$
0^+	1
0^-	.	.	.	1
1^+	.	.	1	.	1	.	.	.
1^-	.	1	.	.	.	1	.	.
2^+	1	.	.	.	1	.	1	.
2^-	.	.	.	1	.	1	.	1
3^+	.	.	1	.	1	.	1	.
3^-	.	1	.	.	.	1	.	1

Types of symmetry labels

- A = Activity (of vibrations, electrons)
- B = Bare rotor (rotations, nuclear spin)
- C = Coupling or Constriction of $A \otimes B$

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

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



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

Angular momentum	atomic label	molecular label
$l=0$	s or S	σ or Σ
$l=1$	p or P	π or Π
$l=2$	d or D	δ or Δ
$l=3$	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	$\Delta_u \dots$
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	$R(\alpha 00)$	$R(-\alpha 180^\circ \alpha)$	I	$I.R(\alpha 00)$	$I.R(-\alpha 180^\circ \alpha)$
$A_{1g} = \Sigma_g^+$	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	$2 \cos \alpha$	0	2	$2 \cos \alpha$	0
$E_{1u} = \pi_u$	2	$2 \cos \alpha$	0	-2	$-2 \cos \alpha$	0
$E_{2g} = \Delta_g$	2	$2 \cos 2\alpha$	0	2	$2 \cos 2\alpha$	0
$E_{2u} = \Delta_u$	2	$2 \cos 2\alpha$	0	-2	$-2 \cos 2\alpha$	0
·	·	·	·	·	·	·
·	·	·	·	·	·	·
·	·	·	·	·	·	·

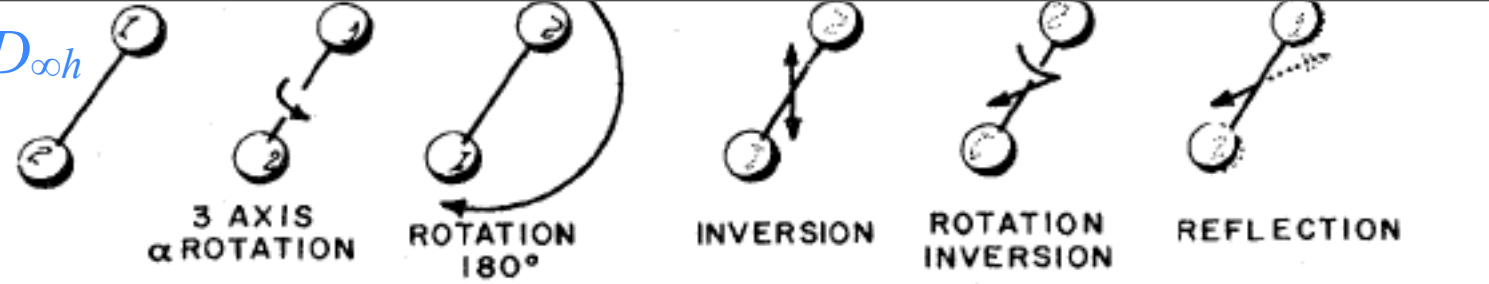
FIG. 15. Characters of $D_{\infty h} = O_{2i}$ symmetry of X_2 rotor.

Types of symmetry labels

- A = Activity (of vibrations, electrons)
- B = Bare rotor (rotations, nuclear spin)
- C = Coupling or Constriction of $A \otimes B$

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

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



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

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

	1	$R(\alpha 00)$	$R(-\alpha 180^\circ \alpha)$	I	$I.R(\alpha 00)$	$I.R(-\alpha 180^\circ \alpha)$
$A_{1g} = \Sigma_g^+$	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	$2 \cos \alpha$	0	2	$2 \cos \alpha$	0
$E_{1u} = \pi_u$	2	$2 \cos \alpha$	0	-2	$-2 \cos \alpha$	0
$E_{2g} = \Delta_g$	2	$2 \cos 2\alpha$	0	2	$2 \cos 2\alpha$	0
$E_{2u} = \Delta_u$	2	$2 \cos 2\alpha$	0	-2	$-2 \cos 2\alpha$	0
⋮	⋮	⋮	⋮	⋮	⋮	⋮

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

$O_3 \backslash O_{2i}$	$B = \Sigma_g^+$	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u	Φ_g	Φ_u	$\Gamma_g \dots$
$N^p = 0^+$	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

A, B, or C Correlations

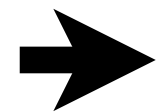
$B =$	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	$\Delta_u \dots$
0^+	1	⋯	⋯	⋯	⋯	⋯	⋯	⋯
0^-	⋯	⋯	⋯	1	⋯	⋯	⋯	⋯
1^+	⋯	⋯	1	⋯	1	⋯	⋯	⋯
1^-	⋯	1	⋯	⋯	⋯	1	⋯	⋯
2^+	1	⋯	⋯	⋯	1	⋯	1	⋯
2^-	⋯	⋯	⋯	1	⋯	1	⋯	1
3^+	⋯	⋯	1	⋯	1	⋯	1	⋯
3^-	⋯	1	⋯	⋯	⋯	1	⋯	1

Types of symmetry labels

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

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

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)

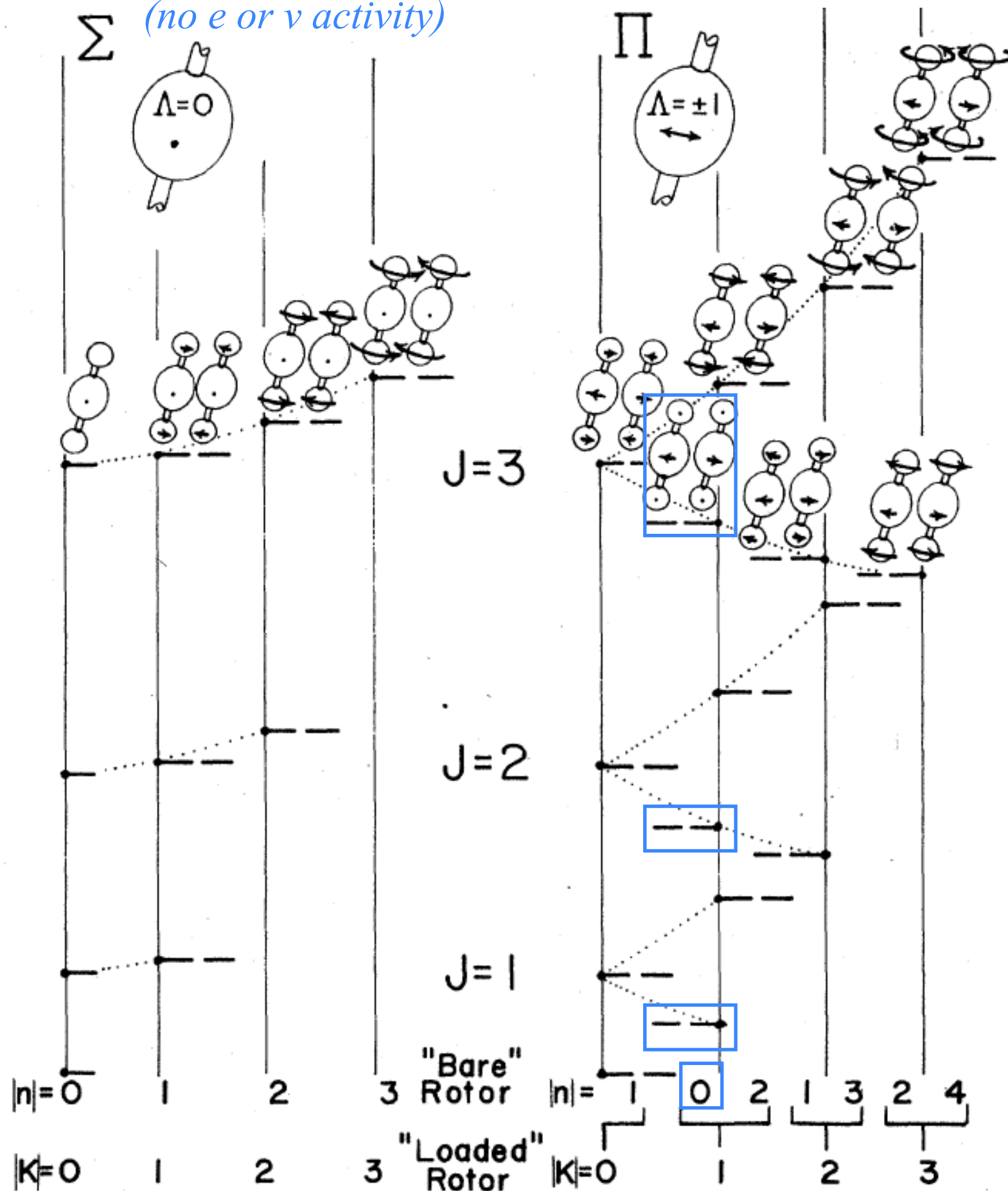


FIG. 18. Σ and Π BOA states for symmetric top molecule. The electronic or vibronic "load" is indicated by an ellipsoid surrounding a "bare" dumb-bell rotor. Arrows indicate the direction of rotation of moving wave states and relative amounts of momentum n or K . Only for the ($n=0, \Pi$) states will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

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

Types of symmetry labels

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

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

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

Simple diatomic examples: Hypothetical C_2 Levels (Bare rotor)

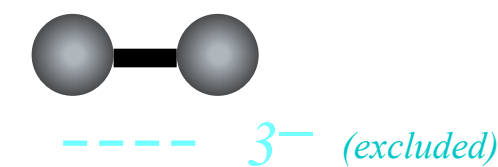
3D Orthogonal group $O(3)$
correlates with $D_{\infty h}$ symmetry

Angular momentum	atomic label	molecular label
$l=0$	s or S	σ or Σ
$l=1$	p or P	π or Π
$l=2$	d or D	δ or Δ
$l=3$	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	$\Delta_u \dots$
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

$^{12}C_2$ Levels



— 2⁺

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

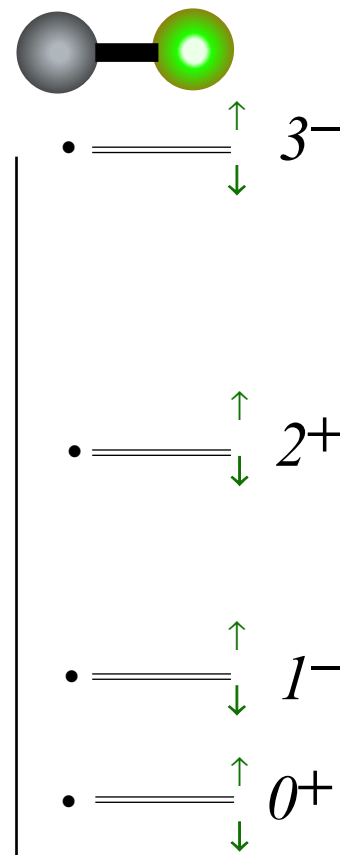
— 0⁺

$B = \Sigma_g^+$

($\boxed{1} \boxed{2} \boxed{\bullet} \boxed{\bullet}$)
orbit, spin-0

Ortho-Species (only)

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



$B = \Sigma$

($\boxed{1} \boxed{2} \boxed{\bullet} \boxed{\downarrow}$)
orbit, spin-0 spin- $\frac{1}{2}$

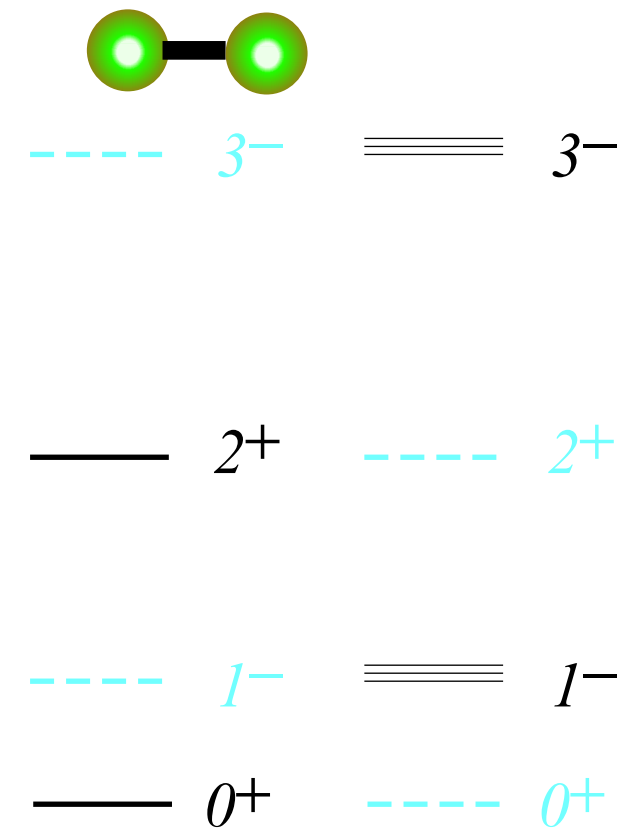
Pairs of Fermi (spin- $\frac{1}{2}$) nuclei required by Pauli principle

to be totally antisymmetric: Either Even-Odd or Odd-Even

^{12}C has zero nuclear spin

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

$^{13}C_2$ Levels



$B = \Sigma_g^+$

($\boxed{1} \boxed{2} \boxed{\uparrow} \boxed{\downarrow}$)
orbit, spin- $\frac{1}{2}$

Para-Species

$B = \Sigma_u^+$

($\boxed{\uparrow} \boxed{\uparrow}$)
($\boxed{1} \boxed{2} \boxed{\uparrow} \boxed{\downarrow}$)
($\boxed{\downarrow} \boxed{\downarrow}$)
orbit, spin- $\frac{1}{2}$

Ortho-Species

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

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

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

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

A, B, or C Correlations

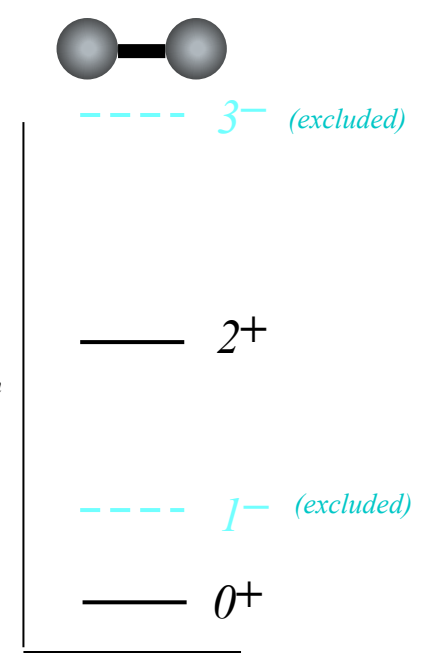
B =	Σ_g^+	Σ_u^+	Σ_g^-	Σ_u^-	Π_g	Π_u	Δ_g	Δ_u ...
0^+	1
0^-	.	.	.	1
1^+	.	.	1	.	1	.	.	.
1^-	.	1	.	.	.	1	.	.
2^+	1	.	.	.	1	.	1	.
2^-	.	.	.	1	.	1	.	1
3^+	.	.	1	.	1	.	1	.
3^-	.	1	.	.	.	1	.	1

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

"Coupled" or "Constricted" Rotor Label C

$C = A \otimes B = \Sigma_u^+ \otimes \Sigma_g^+ = \Sigma_u^+$

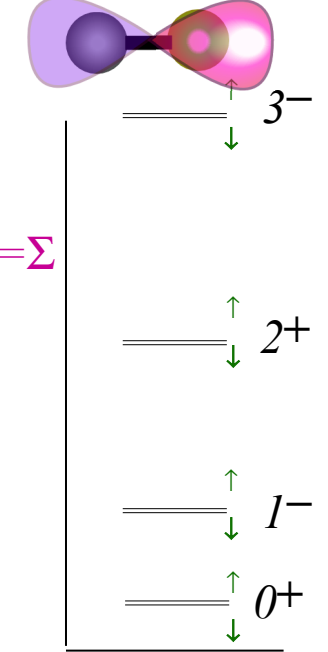
$^{12}C_2$ Ground Levels



"Bare" Rotor Label $B = \Sigma_g^+$

($\boxed{1} \boxed{2} \quad \boxed{\cdot} \boxed{\cdot}$) orbit, spin-0 Ortho Species (only)

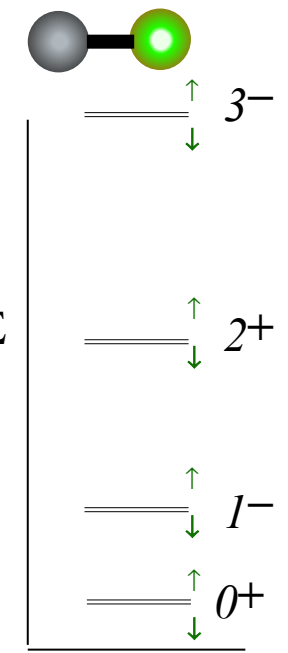
$^{12}C^{13}C \Sigma$ Excited Levels



$A = \Sigma$

$C = \Sigma$

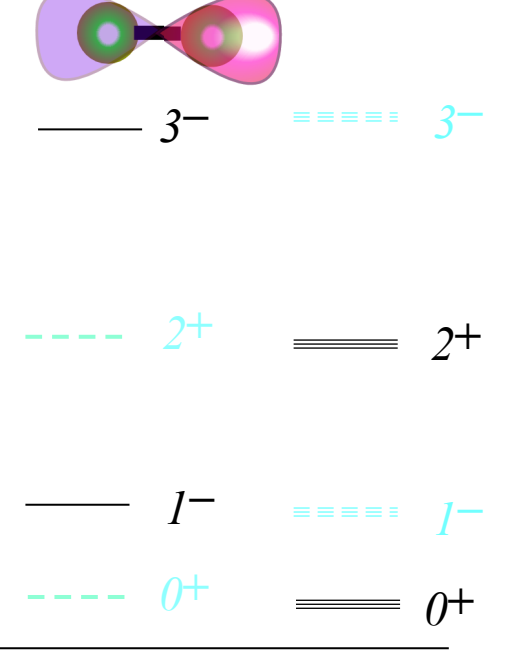
$^{12}C^{13}C$ Ground Levels



$A = \Sigma$

$B = \Sigma$
($\boxed{1} \boxed{2} \quad \boxed{\uparrow} \boxed{\downarrow}$) orbit, spin-0 spin-1/2

$^{13}C_2 \Sigma_u^+$ Excited Levels

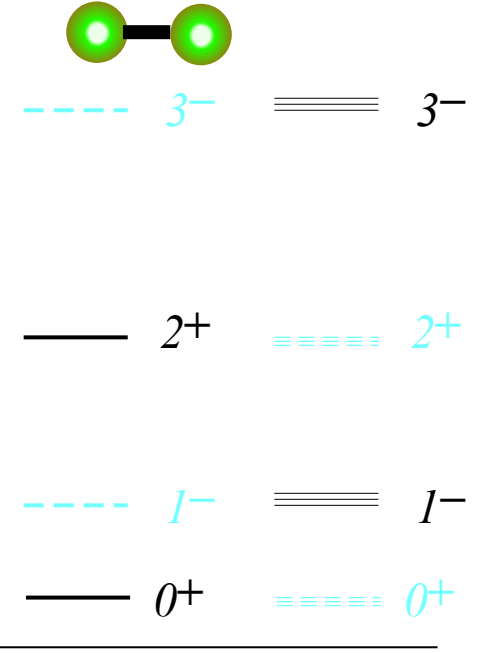


$A = \Sigma_u^+$

$C = \Sigma_u^+$

$C = \Sigma_g^+$

$^{13}C_2$ Ground Levels



$B = \Sigma_g^+$

$B = \Sigma_u^+$

($\boxed{1} \boxed{2} \quad \boxed{\uparrow} \boxed{\downarrow}$) orbit, spin

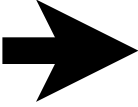
($\boxed{1} \quad \boxed{\uparrow \uparrow}$
 $\boxed{2} \quad \boxed{\uparrow \downarrow}$
 $\quad \quad \boxed{\downarrow \downarrow}$) orbit, spin-1/2

Para-Species

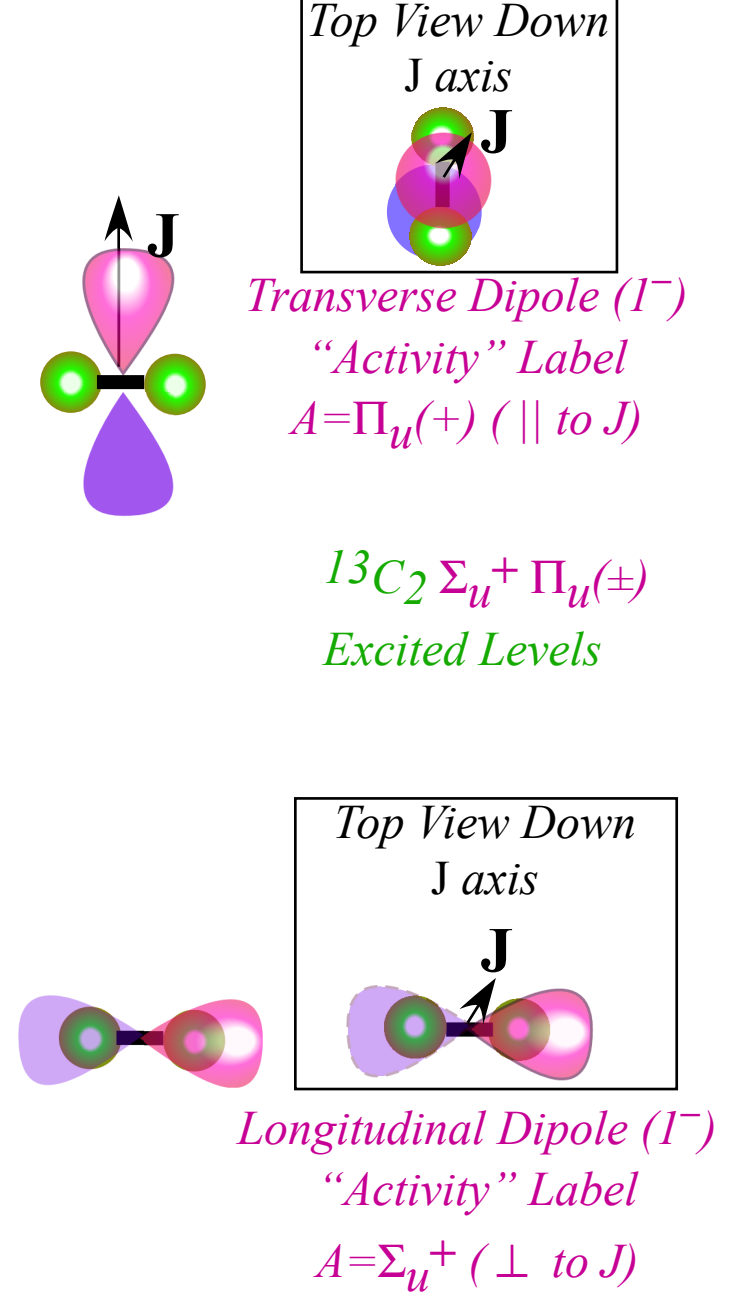
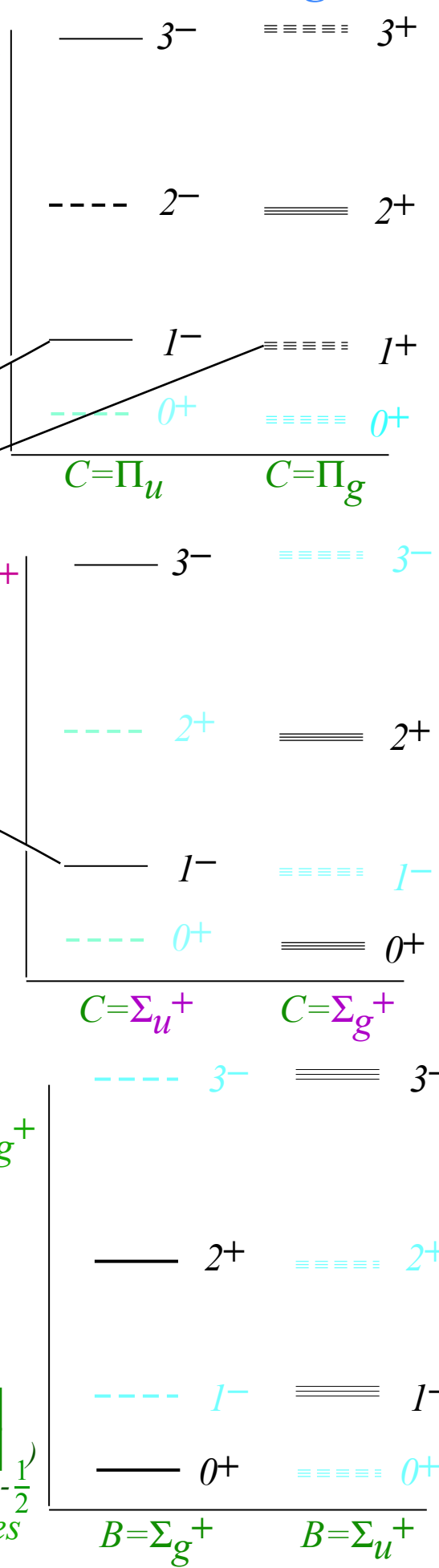
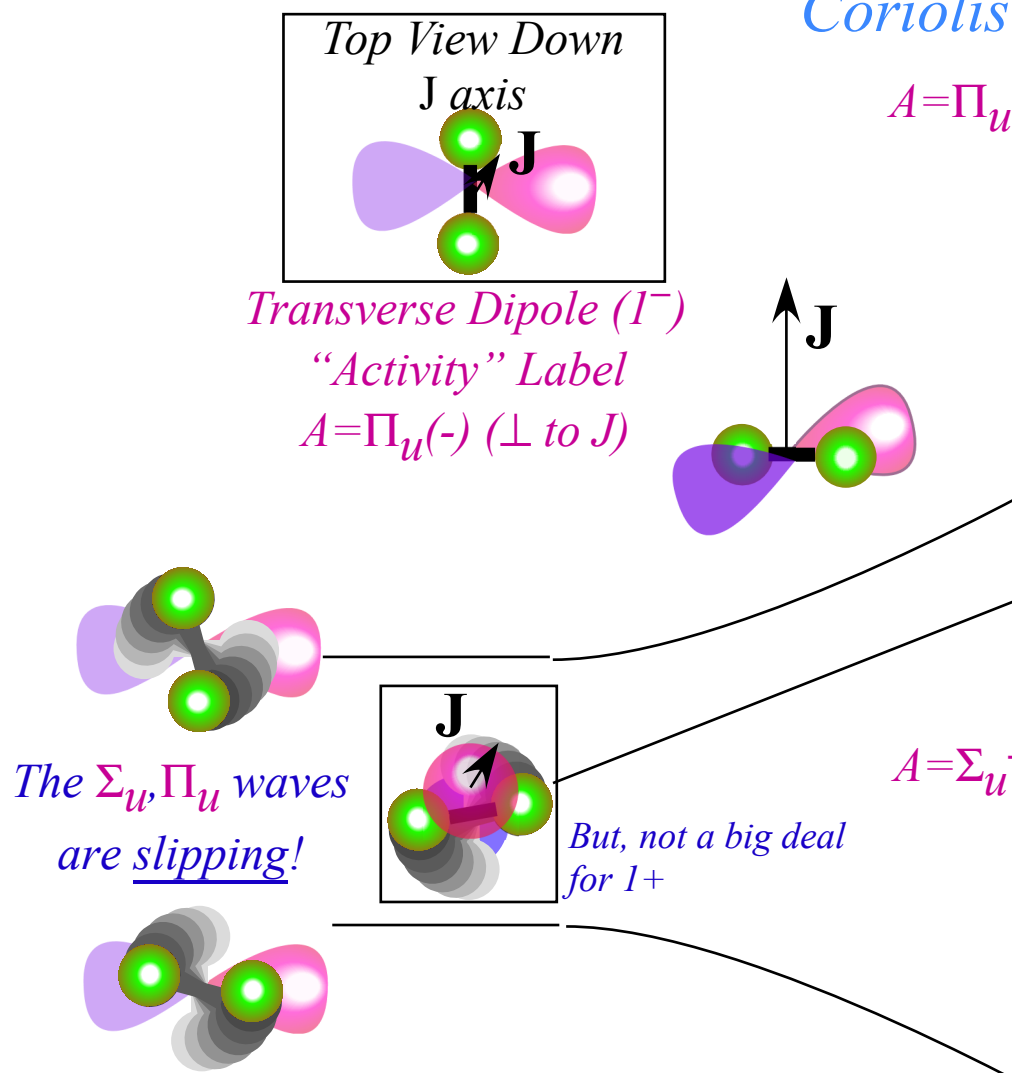
Ortho-Species

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

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

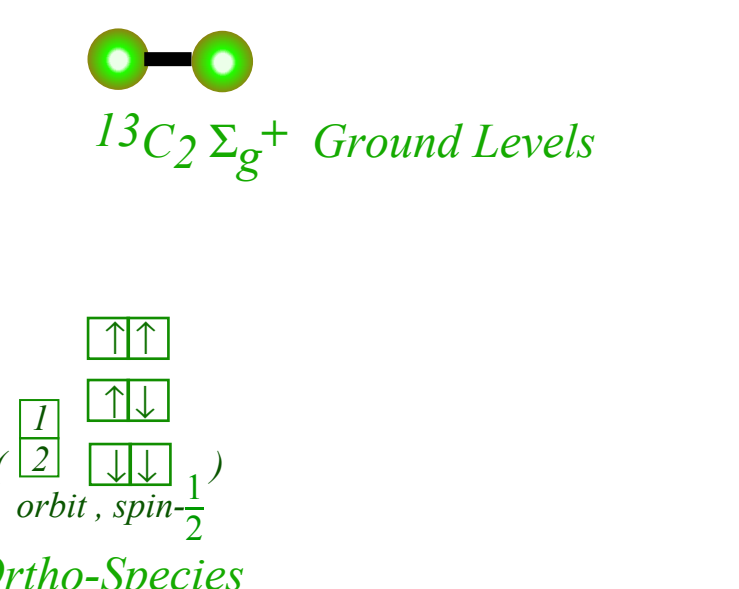
 *Coriolis and λ -doubling levels*
Dipole-allowed transitions

Coriolis and λ -doubling levels



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



Diatomic or linear molecule: Coriolis and λ-doubling levels

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

$$\langle \mathbf{H} \rangle = \begin{vmatrix} \epsilon_{\Sigma} + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_{\pi} + 2 & 0 \\ 0 & 0 & \epsilon_{\pi} + 2 \end{vmatrix} / 2I_{\bar{x}\bar{y}} \quad (J=1)\text{-case}$$

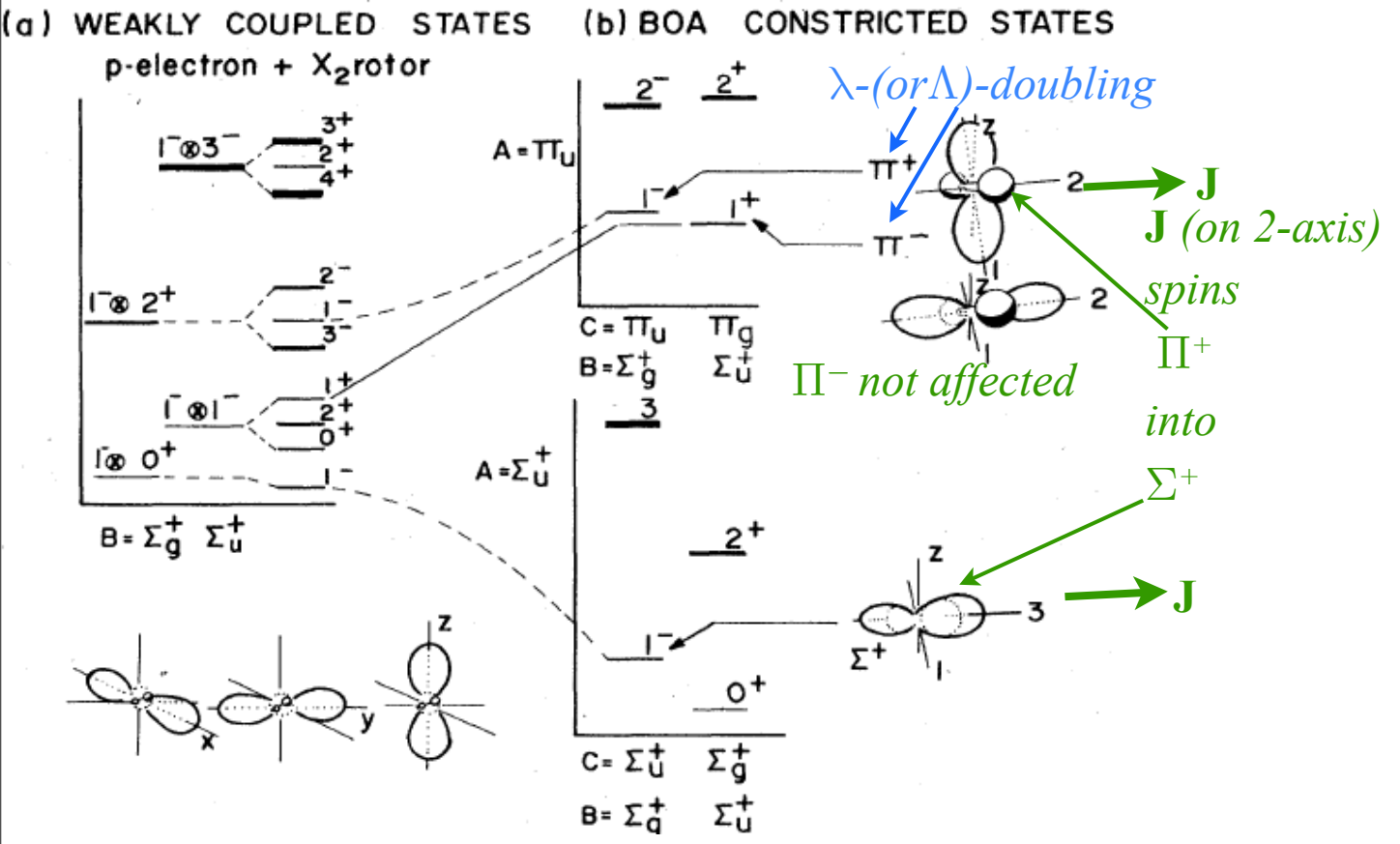


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P , B , and J^P are good labels.) (b) BOA-constricted states. (A , B , C , and J^P are good labels.) States with the same $B = \Sigma_g^+$ and $J^P = 1^-$ are connected by dotted lines. 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

$$\langle H \rangle = \begin{bmatrix} J(J+1)+2 & -2(J(J+1))^{1/2} & 0 \\ -2(J(J+1))^{1/2} & \epsilon_\pi + J(J+1) & 0 \\ 0 & 0 & \epsilon_\pi + J(J+1) \end{bmatrix}$$

$$H = H_e + (J^2 + L^2 - 2J_x L_x - 2J_y L_y - 2J_z L_z) / 2I_{xy}$$

$$\langle H \rangle = \begin{bmatrix} \epsilon_\Sigma + 4 & -2\sqrt{2} & 0 \\ -2\sqrt{2} & \epsilon_\pi + 2 & 0 \\ 0 & 0 & \epsilon_\pi + 2 \end{bmatrix} / 2I_{xy} \quad (J=1)\text{-case}$$

(a) WEAKLY COUPLED STATES (b) BOA CONSTRICTED STATES

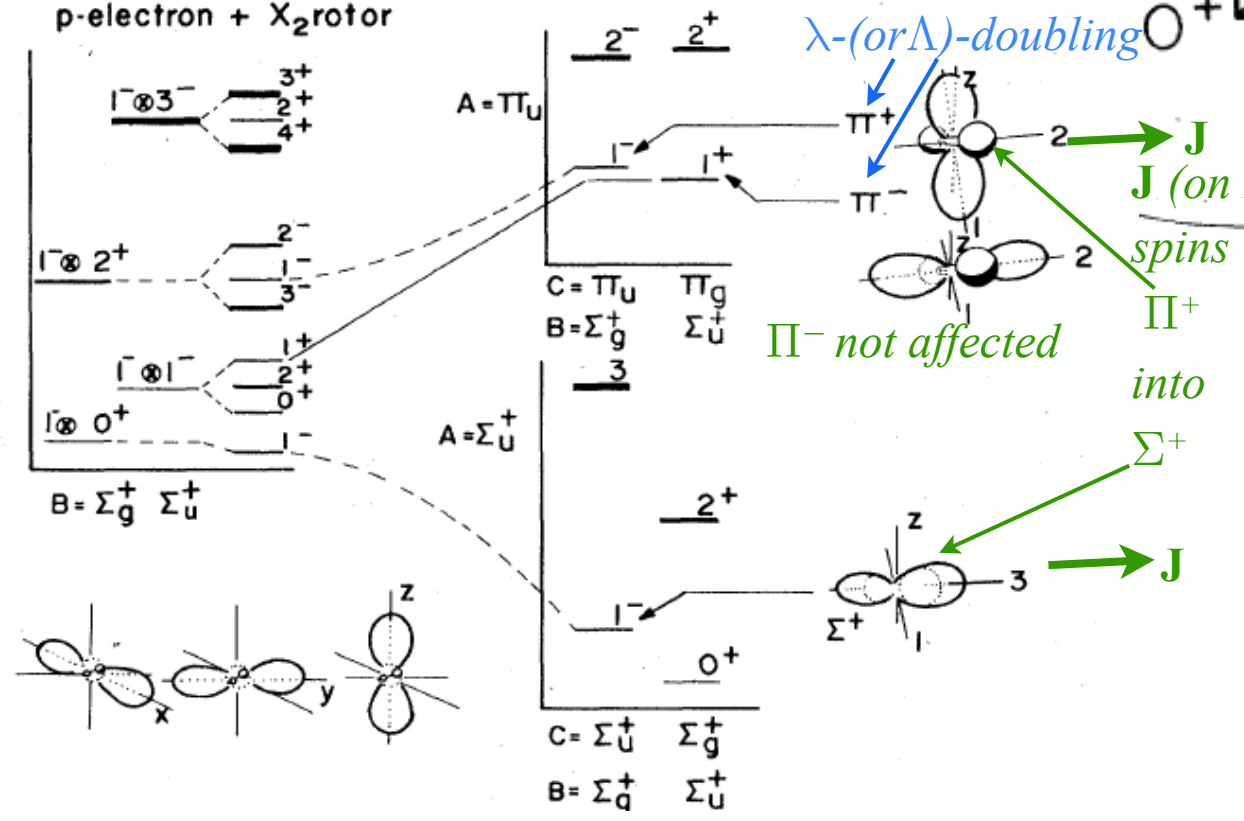


FIG. 19. Correlation diagram for $l=1$ electronic states in the presence of an X_2 rotor. (a) Weakly-coupled states. (N^P , B , and J^P are good labels.) (b) BOA-constricted states. (A , B , C , and J^P are good labels.) States with the same $B = \Sigma_g^+$ and $J^P = 1^-$ are connected by dotted lines. 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.

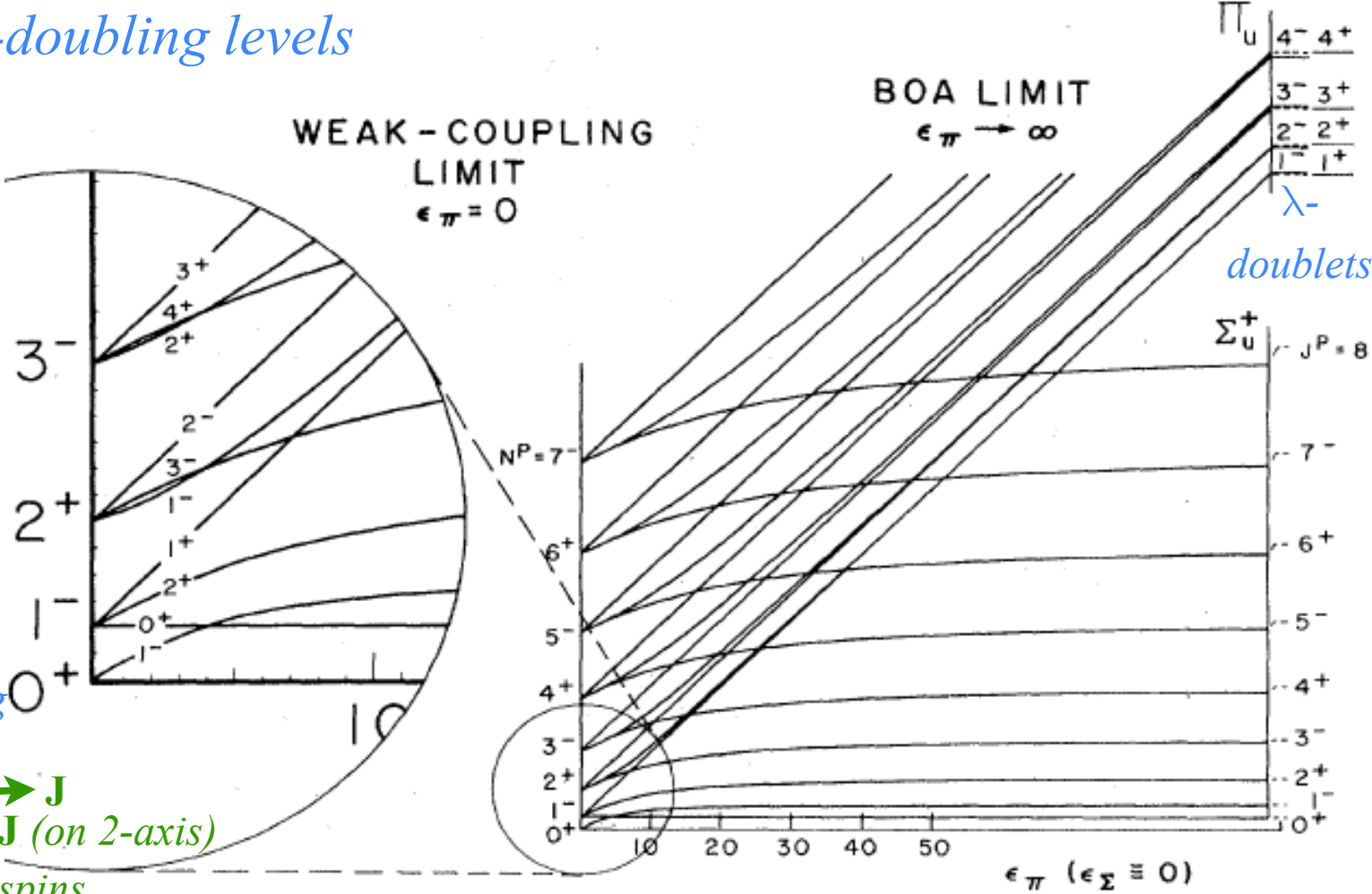


FIG. 20. ($n=0$) J -level plots ($J=0-8$) for ($l=1$: Σ, Π) as functions of electronic energy difference (ϵ_π). The right-hand side of the figure shows the separate Π and Σ manifolds that will arise in the BOA limit as $\epsilon_\pi \rightarrow \infty$. (In this figure we set $\epsilon_\Sigma = 0$, and let the rotational constant $B_v = 1/I_{xy}$ 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 $J=N\pm 1$ 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 $J=(N\pm 1)$ 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.

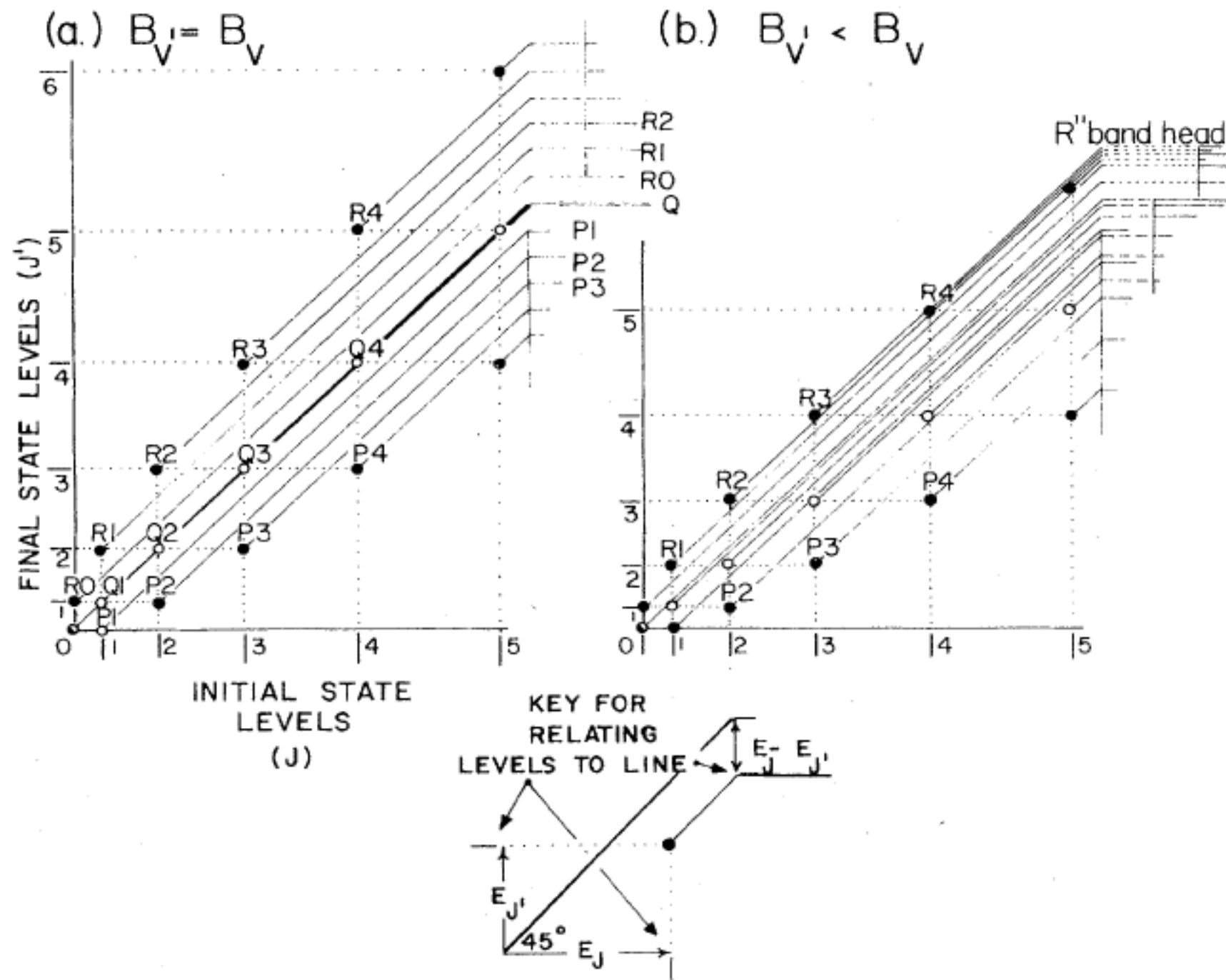
Diatomic or linear molecule symmetry $O(3) \supset D_{\infty h} \supset C_{\infty v}$

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

Coriolis and λ -doubling levels

 *Dipole-allowed transitions*

Diatomic or linear molecule: Dipole-allowed transitions



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

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

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

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

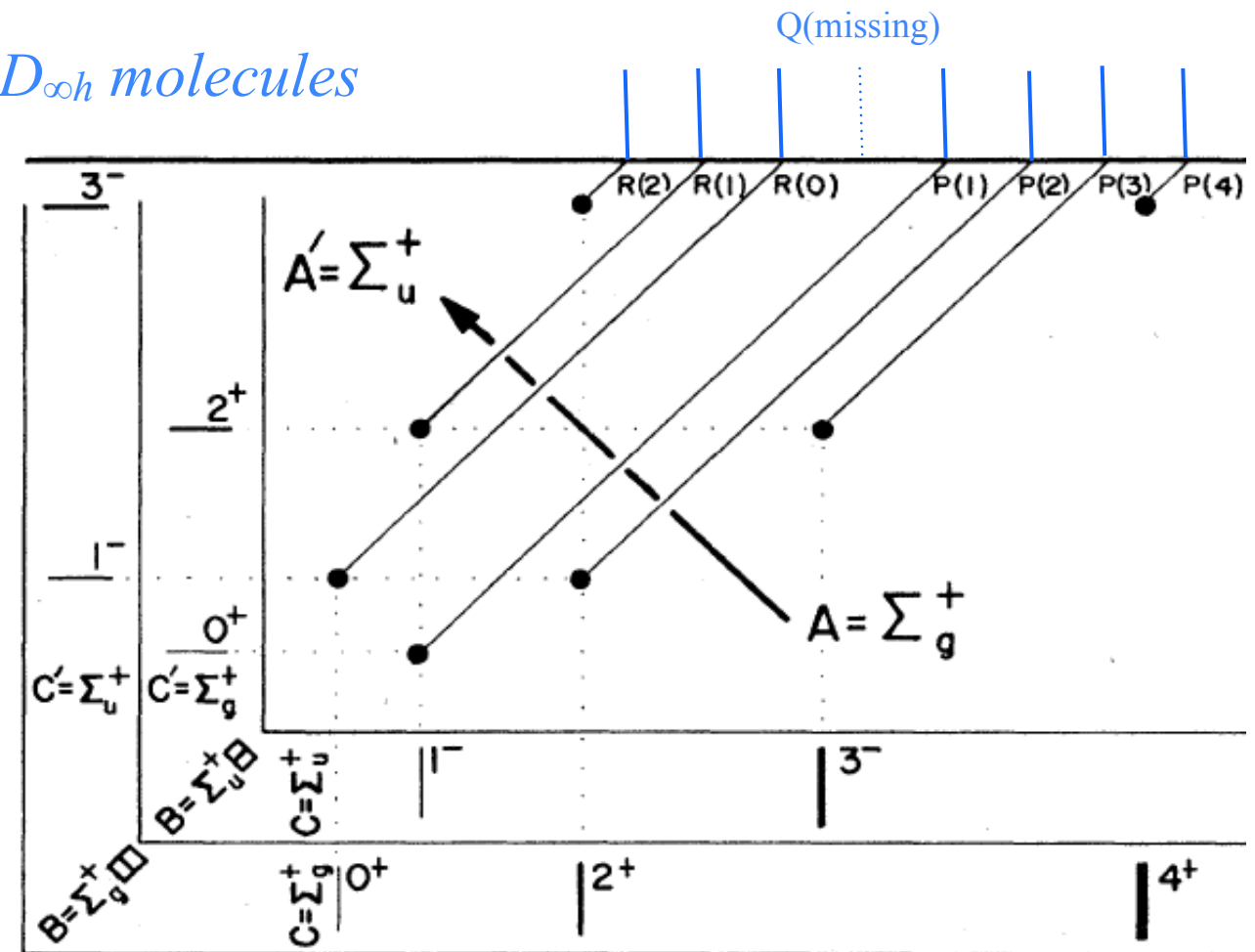
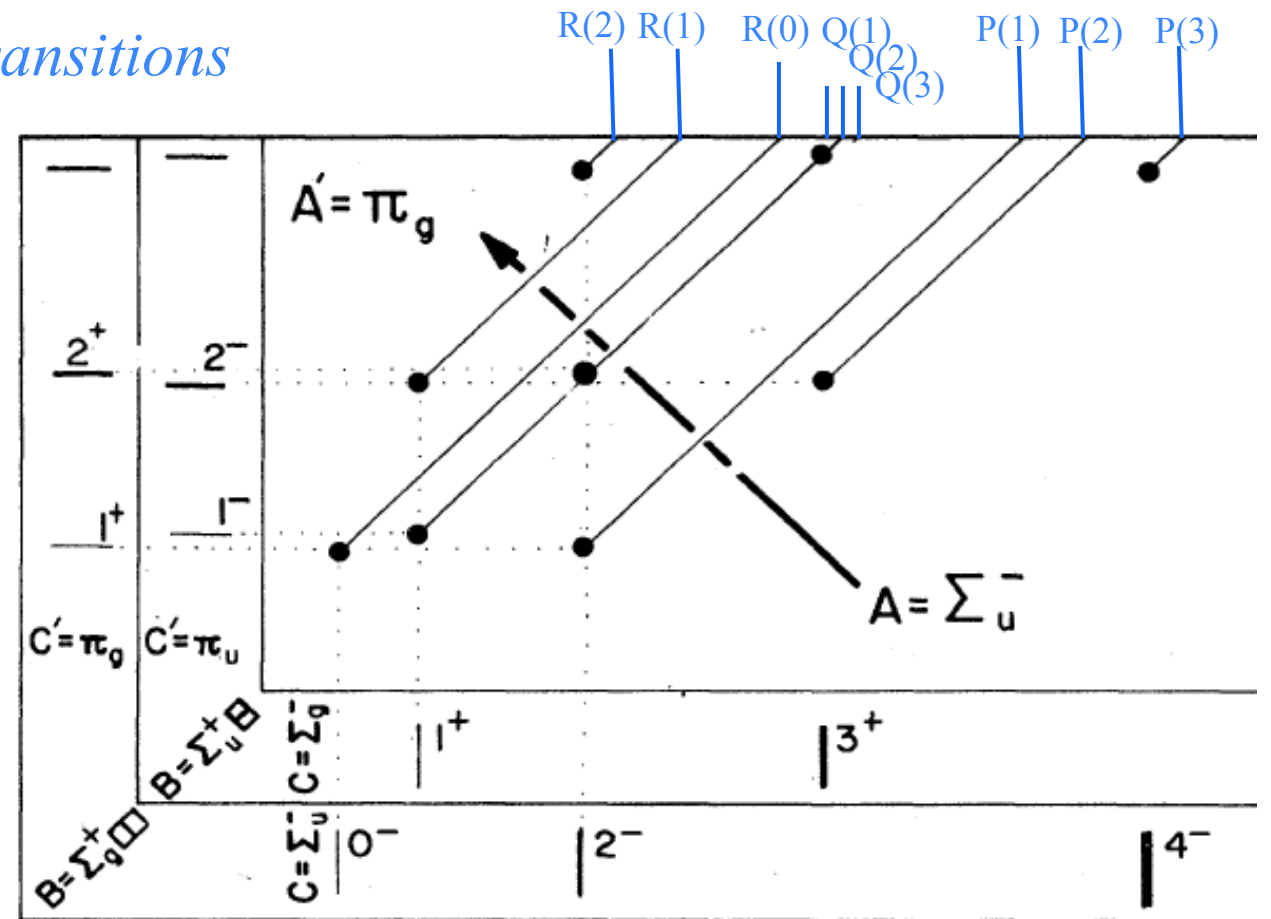


FIG. 31. Electric dipole transitions in linear symmetric (O_{2i}) molecules X_2, XYX, \dots (a) $\Sigma_g^+ \rightarrow \Sigma_u^+$. (b) $\Sigma_u^- \rightarrow \Pi_g$. Transitions are only allowed between levels lying in the same B corridor. Note that the ($\Sigma_u^- \rightarrow \Pi_g$) Q branch is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

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

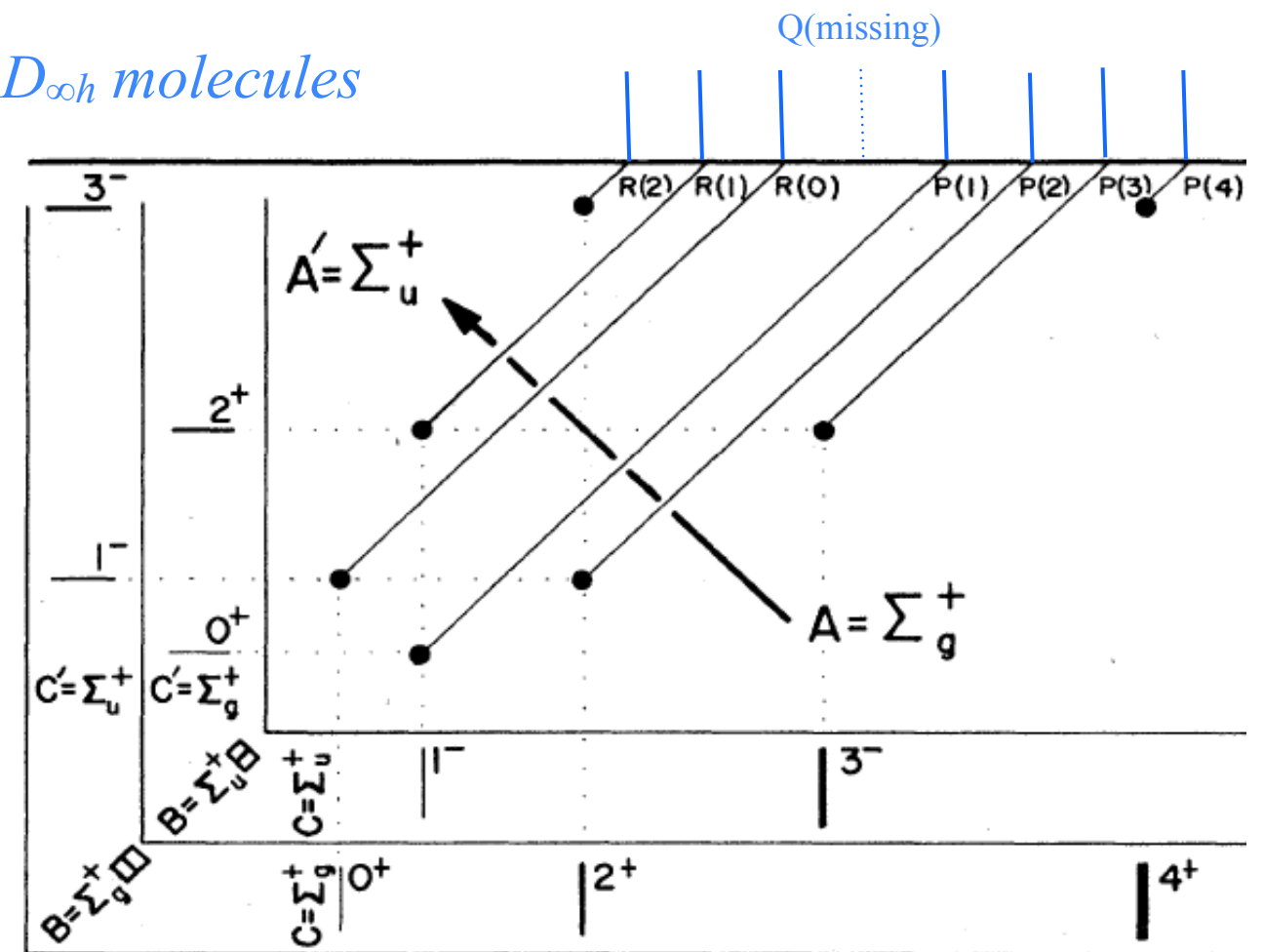


FIG. 31. Electric dipole transitions in linear symmetric (O_{2i}) molecules X_2, XYX, \dots (a) $\Sigma_g^+ \rightarrow \Sigma_u^+$. (b) $\Sigma_u^- \rightarrow \Pi_g$. Transitions are only allowed between levels lying in the same B corridor. Note that the ($\Sigma_u^- \rightarrow \Pi_g$) Q branch is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

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

(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\square\rangle = |B = \Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

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

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

ORBITAL		SPIN	ORBITAL		SPIN
$\square\square$	$\square\square$	n=2	$\square\square$	\square	\square
\square	\square		\square	$\square\square$	

S_2

A_1	$\begin{matrix} 1 & 2 \end{matrix}$	$(1)(2)$	$\begin{matrix} 1 & 1 \end{matrix}$
A_2	$\begin{matrix} 1 \\ 2 \end{matrix}$	(12)	$\begin{matrix} 1 & -1 \end{matrix}$

C_2

$\mathbf{1}$	σ
A_1	$\begin{matrix} 1 & 1 \end{matrix}$
A_2	$\begin{matrix} 1 & -1 \end{matrix}$



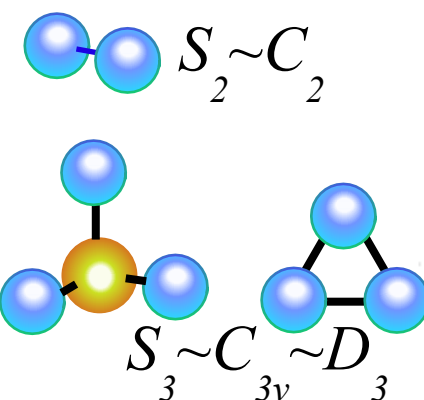
(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\square\rangle = |B = \Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

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

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

(a) BOSE NUCLEI			(b) FERMI NUCLEI	
ORBITAL	SPIN		ORBITAL	SPIN
n=2				
$\square\square$	$\square\square$		$\square\square$	\square
\square	\square		\square	$\square\square$
n=3				
$\square\square\square$	$\square\square\square$		$\square\square\square$	\square
\square	\square		\square	\square
\square	\square		\square	\square
\square	\square		\square	\square



group S_n is equivalent to \mathcal{G}

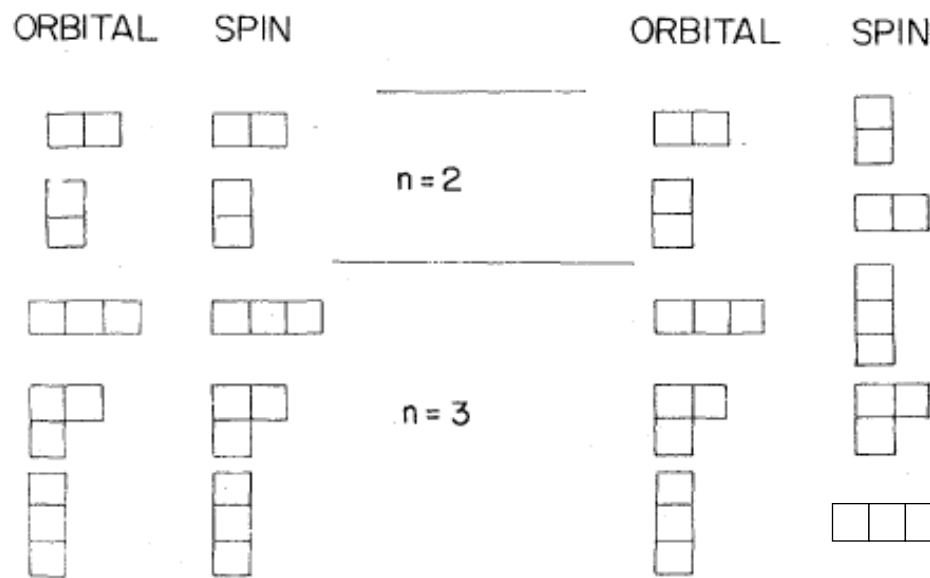
S_2	C_2
A_1 $\begin{bmatrix} 1 & 2 \end{bmatrix}$ A_2 $\begin{bmatrix} 1 \\ 2 \end{bmatrix}$	$\mathbf{1}$ σ A_1 $\begin{bmatrix} 1 & 1 \end{bmatrix}$ A_2 $\begin{bmatrix} 1 & -1 \end{bmatrix}$
S_3 A_1 $\begin{bmatrix} 1 & 2 & 3 \end{bmatrix}$ A_2 $\begin{bmatrix} 1 \\ 2 \\ 3 \end{bmatrix}$ E $\begin{bmatrix} 1 & 2 \\ 3 \end{bmatrix}$	$\mathbf{1}$ \mathbf{r}^1 σ_1 σ_2 σ_3 A_1 $\begin{bmatrix} 1 & 1 & 1 \end{bmatrix}$ A_2 $\begin{bmatrix} 1 & 1 & -1 \end{bmatrix}$ E $\begin{bmatrix} 2 & -1 & 0 \end{bmatrix}$

(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\square\rangle = |B = \Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

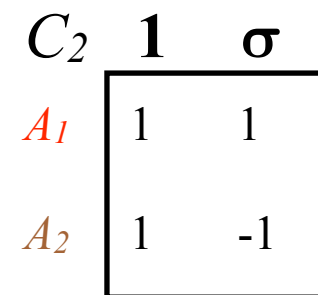
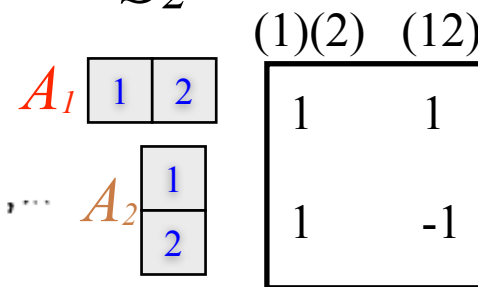
FIG. 26. Orbital and spin tableaus used to label homonuclear n -atomic molecules ($n=2,3,4,\dots$).

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

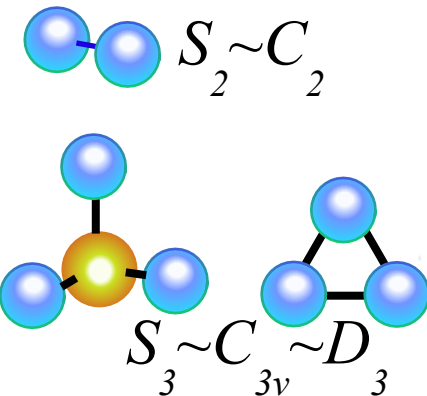
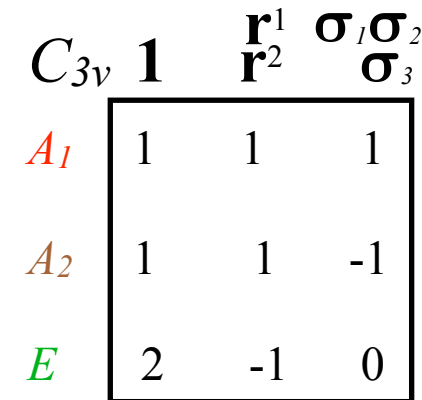
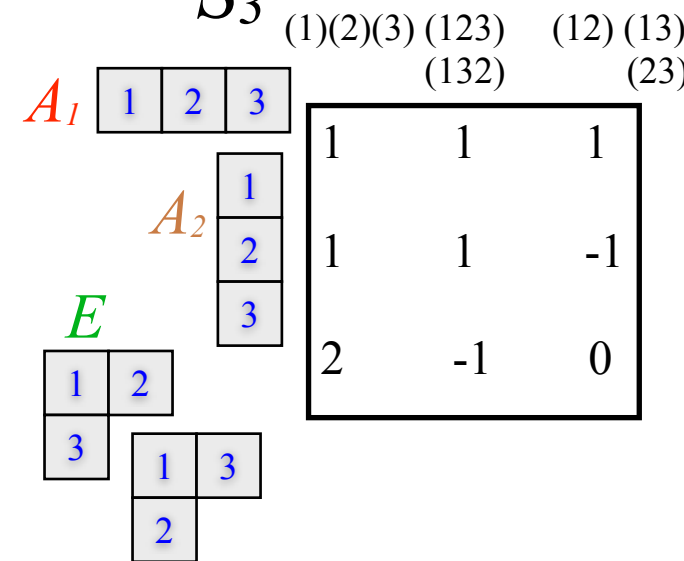


group S_n is equivalent to \mathcal{G}

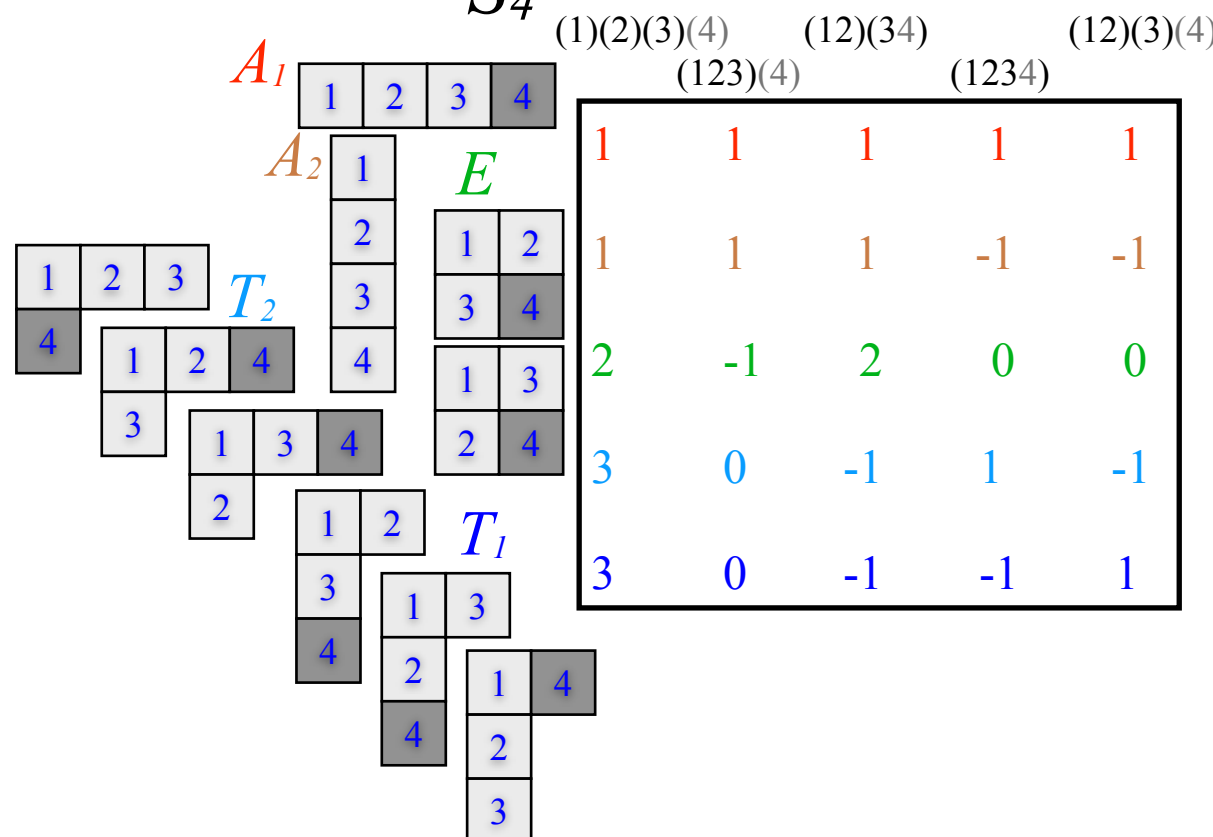
S_2



S_3

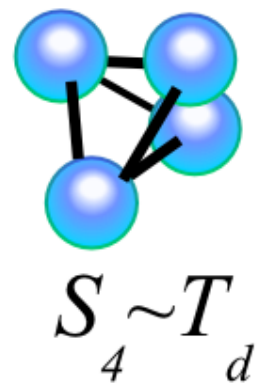


S_4



Tetrahedral: $\mathcal{G} = T_d$

T_d	$\mathbf{1}$	$\mathbf{r}_{1..4}$	180° ρ_{xyz}	90° \mathbf{R}_{xyz}	180° $\sigma_{1..6}$
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



(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\square\rangle = |B = \Sigma_u^+\rangle$

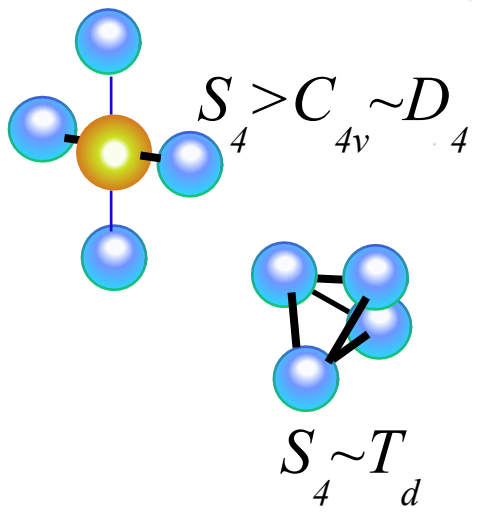
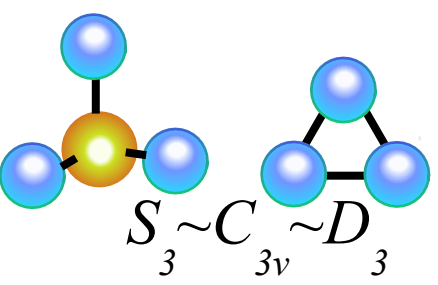
FIG. 25. Orbital tableau labeling of a homonuclear diatomic

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

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

ORBITAL SPIN ORBITAL SPIN

ORBITAL	SPIN		ORBITAL	SPIN
$\square\square$	$\square\square$	n=2	$\square\square$	\square
\square	\square		\square	$\square\square$
$\square\square\square$	$\square\square\square$	n=3	$\square\square\square$	\square
\square	\square		\square	\square
\square	\square		\square	\square
\square	\square		\square	\square
$\square\square\square\square$	$\square\square\square\square$	n=4	$\square\square\square\square$	\square
\square	\square		\square	\square
\square	\square		\square	\square
\square	\square		\square	\square
\square	\square		\square	\square
\square	\square		\square	\square



S_2

(1)(2) (12)

A_1 $\begin{bmatrix} 1 & 2 \\ 1 & 1 \end{bmatrix}$

A_2 $\begin{bmatrix} 1 & 2 \\ 1 & -1 \end{bmatrix}$

C_2 $\mathbf{1} \quad \sigma$

A_1 $\begin{bmatrix} 1 & 1 \\ 1 & 1 \end{bmatrix}$

A_2 $\begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}$

S_3

(1)(2)(3) (123) (12)(13) (132) (23)

A_1 $\begin{bmatrix} 1 & 2 & 3 \\ 1 & 1 & 1 \end{bmatrix}$

A_2 $\begin{bmatrix} 1 & 2 & 3 \\ 1 & 1 & -1 \\ 2 & -1 & 0 \end{bmatrix}$

E $\begin{bmatrix} 1 & 2 \\ 3 & 3 \end{bmatrix}$

C_{3v} $\mathbf{1} \quad \mathbf{r}^1 \quad \sigma_1 \quad \sigma_2 \quad \sigma_3$

A_1 $\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & 1 \end{bmatrix}$

A_2 $\begin{bmatrix} 1 & 1 & 1 \\ 1 & 1 & -1 \end{bmatrix}$

E $\begin{bmatrix} 2 & -1 & 0 \\ 2 & -1 & 0 \end{bmatrix}$

S_4

(1)(2)(3)(4) (12)(34) (123)(4) (12)(3)(4) (1234)

A_1 $\begin{bmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & 1 \end{bmatrix}$

A_2 $\begin{bmatrix} 1 & 2 & 3 & 4 \\ 1 & 1 & 1 & -1 \\ 2 & -1 & 2 & 0 \\ 3 & 0 & -1 & 1 \\ 3 & 0 & -1 & -1 \end{bmatrix}$

E $\begin{bmatrix} 1 & 2 \\ 3 & 4 \end{bmatrix}$

T_2 $\begin{bmatrix} 1 & 2 & 3 \\ 4 & 4 & 4 \end{bmatrix}$

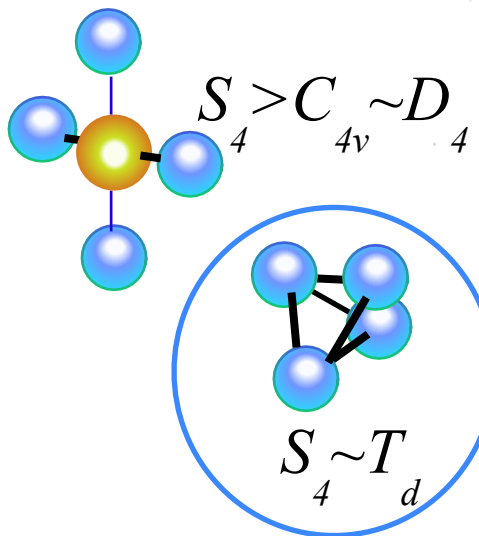
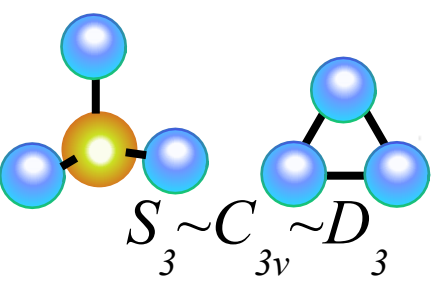
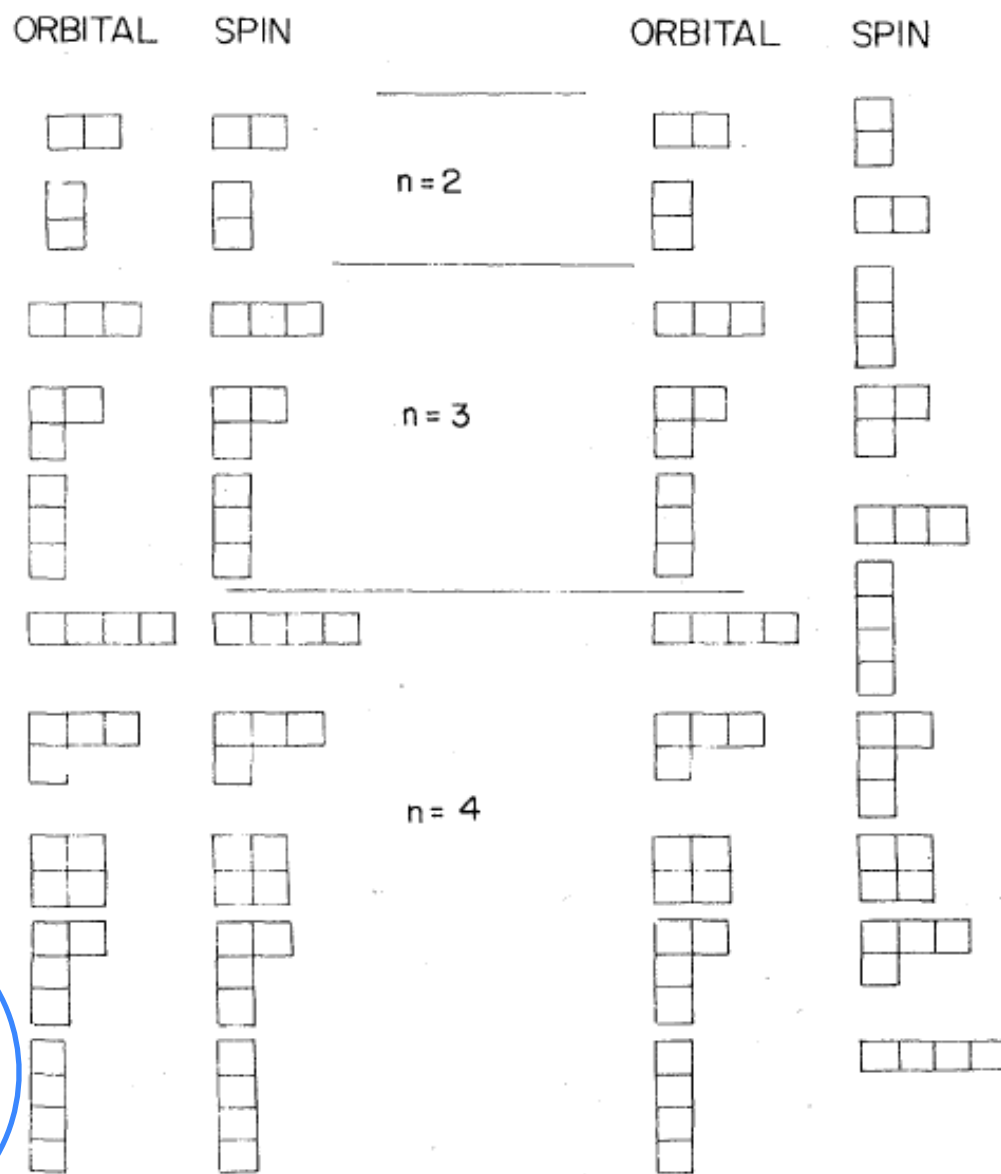
T_1 $\begin{bmatrix} 1 & 2 \\ 3 & 3 \\ 4 & 4 \end{bmatrix}$

(a) $|\square\square\rangle = |B = \Sigma_g^+\rangle$ (b) $|\square\rangle = |B = \Sigma_u^+\rangle$

FIG. 25. Orbital tableau labeling of a homonuclear diatomic

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

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



Methane-like: XY_4

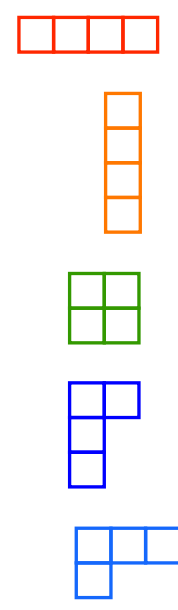


TABLE XIII. T_d characters and symmetry.

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}
$(L_x L_y L_z) F_1$	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. $O_3 + T_d$ 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
5^*	1	2	1	5^-	...	1	2	1
6^*	1	1	1	1	2	6^-	1	1	1	2
7^*	...	1	1	2	2	7^-	...	1	2	2

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

S_n Young Tableau irrep dimension formula

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

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

Examples:

$$\ell^{A_1} = \ell^{[3,0,0]}(S_3) = \frac{3 \cdot 2 \cdot 1}{\begin{array}{|c|c|c|} \hline 3 & 2 & 1 \\ \hline \end{array}} = 1$$

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

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

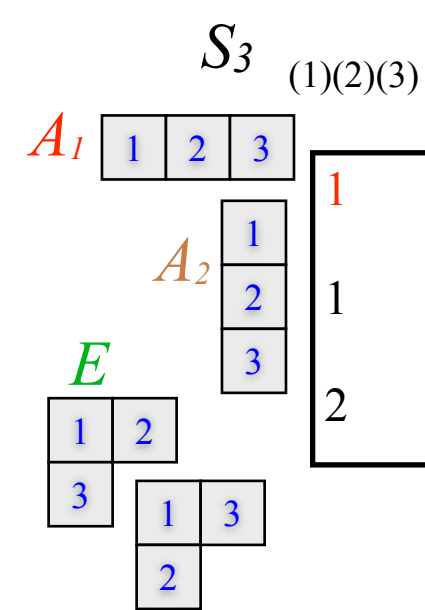


FIG. 28. Robinson formula for statistical weights. The “hook-length” of a box in the tableau is the number of boxes in a “hook” which includes that box and all boxes in the line to the right and in the column below it.

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

<i>m</i>	<i>m+1</i>	<i>m+2</i>	<i>m+3</i>	<i>m+4</i>
<i>m-1</i>	<i>m</i>	<i>m+1</i>		
<i>m-2</i>	<i>m-1</i>			
<i>m-3</i>				

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

Examples:

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

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

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

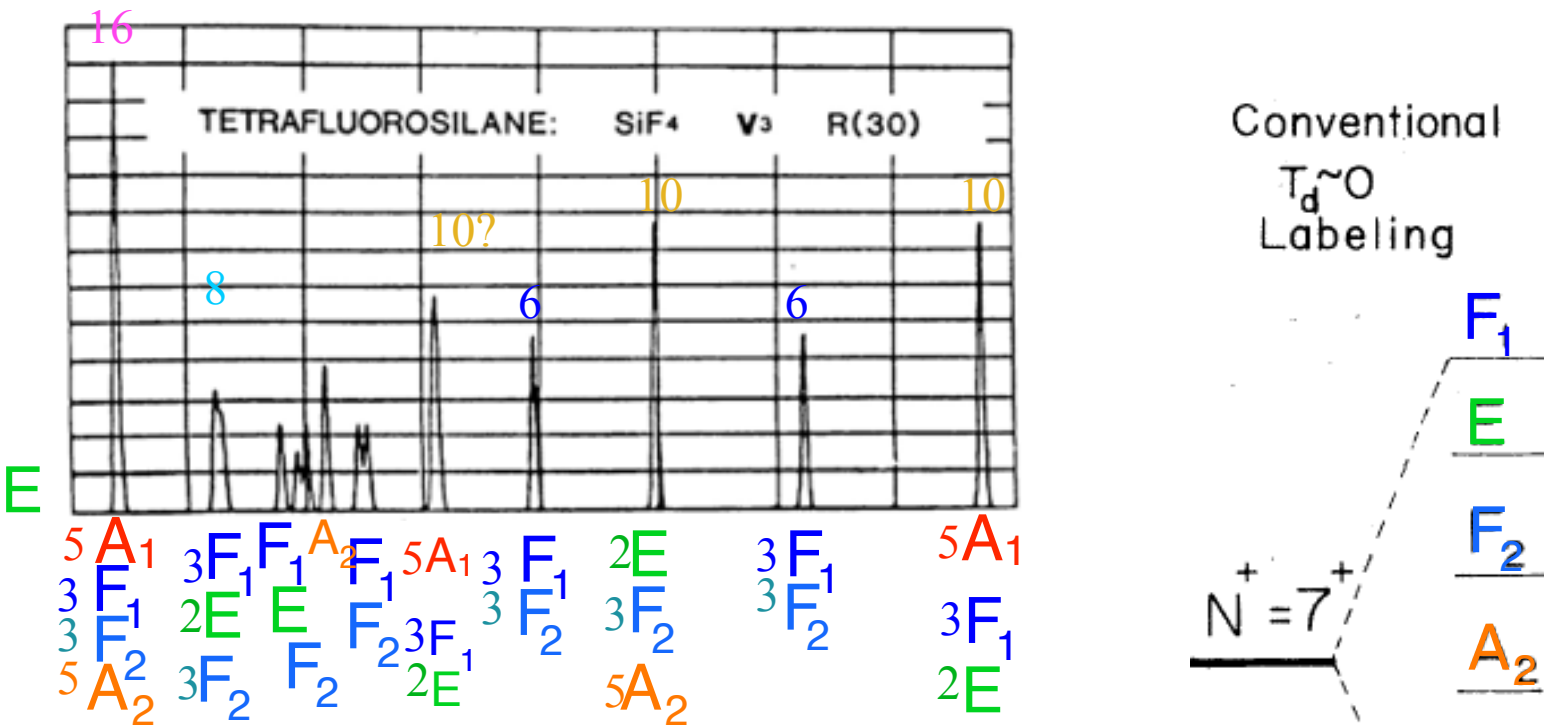


FIG. 28. Robinson formula for statistical weights. The "hook-length" of a box in the tableau is the number of boxes in a "hook" which includes that box and all boxes in the line to the right and in the column below it.

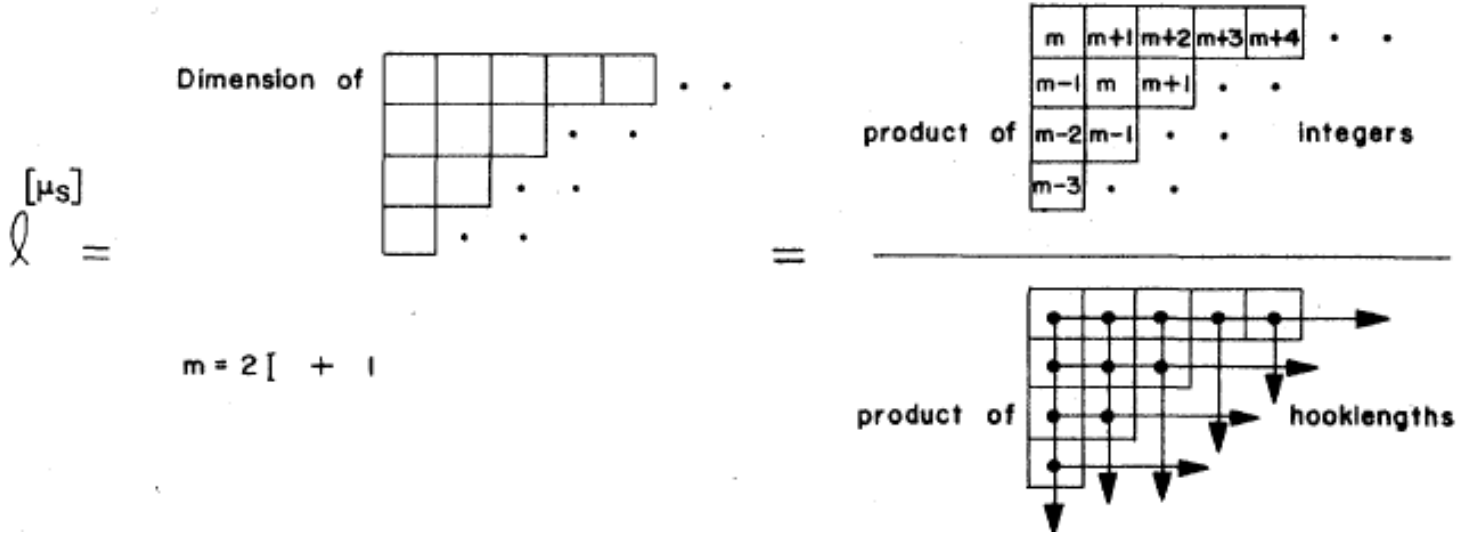
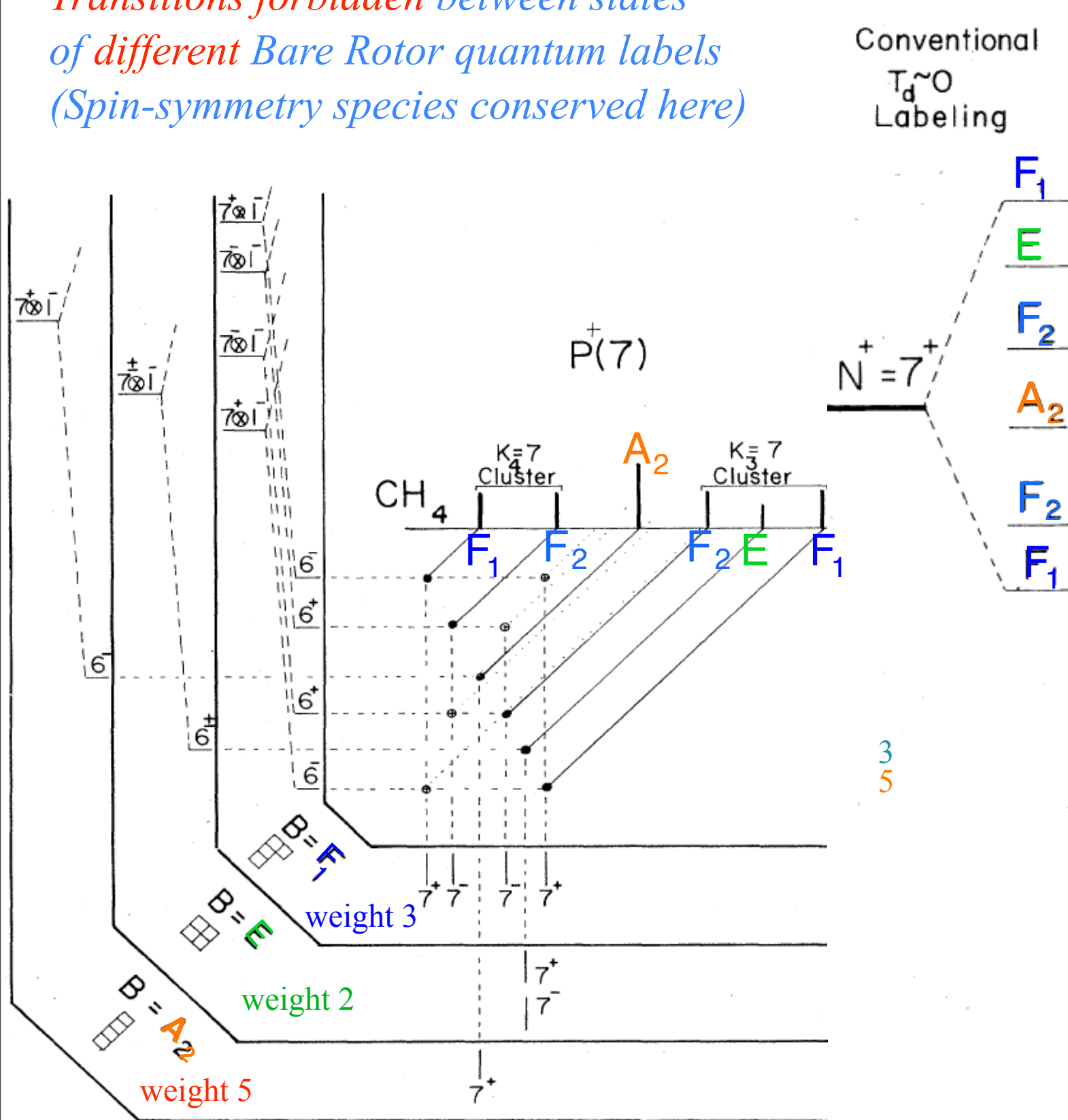


FIG. 36. Comparison of conventional CH_4 labeling with present labeling. The latter shows clearly the "hidden" structure of inversion doublets which has a structure very much like that of NH_3 . For CH_4 , however, only the E levels are actually double according to the statistical weight calculations.

	Present Complete T_d Labeling				
	7^-	7^+	7^+ 7^-	7^+	7^-
F_1					
E					
F_2					
A_2	7^-	7^+			
F_2				7^-	7^+
F_1				7^+	7^-
$B = A_1$	\square				
A_2	$\begin{matrix} \square \\ \square \\ \square \end{matrix}$				
E	$\begin{matrix} \square & \square \\ \square & \square \end{matrix}$				
F_1	$\begin{matrix} \square \\ \square \\ \square \end{matrix}$				
F_2	$\begin{matrix} \square & \square \\ \square & \square \end{matrix}$				
CD_4	$\frac{3 \cdot 4 \cdot 5 \cdot 6}{4 \cdot 3 \cdot 2 \cdot 1} = 15$	$\frac{3}{2} / \frac{4}{3} = 0$	$\frac{3 \cdot 4}{3 \cdot 2} = 6$	$\frac{3 \cdot 4}{2 \cdot 1} = 3$	$\frac{3 \cdot 4 \cdot 5}{4 \cdot 2 \cdot 1} = 15$
CH_4	$\frac{2}{1} / \frac{4}{3} = 0$	$\frac{2 \cdot 3 \cdot 4 \cdot 5}{4 \cdot 3 \cdot 2 \cdot 1} = 5$	$\frac{2 \cdot 3}{3 \cdot 2} = 1$	$\frac{2 \cdot 3 \cdot 4}{4 \cdot 2 \cdot 1} = 3$	$\frac{2 \cdot 3}{0 / 2} = 0$
Statistical Weight Calculations					

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

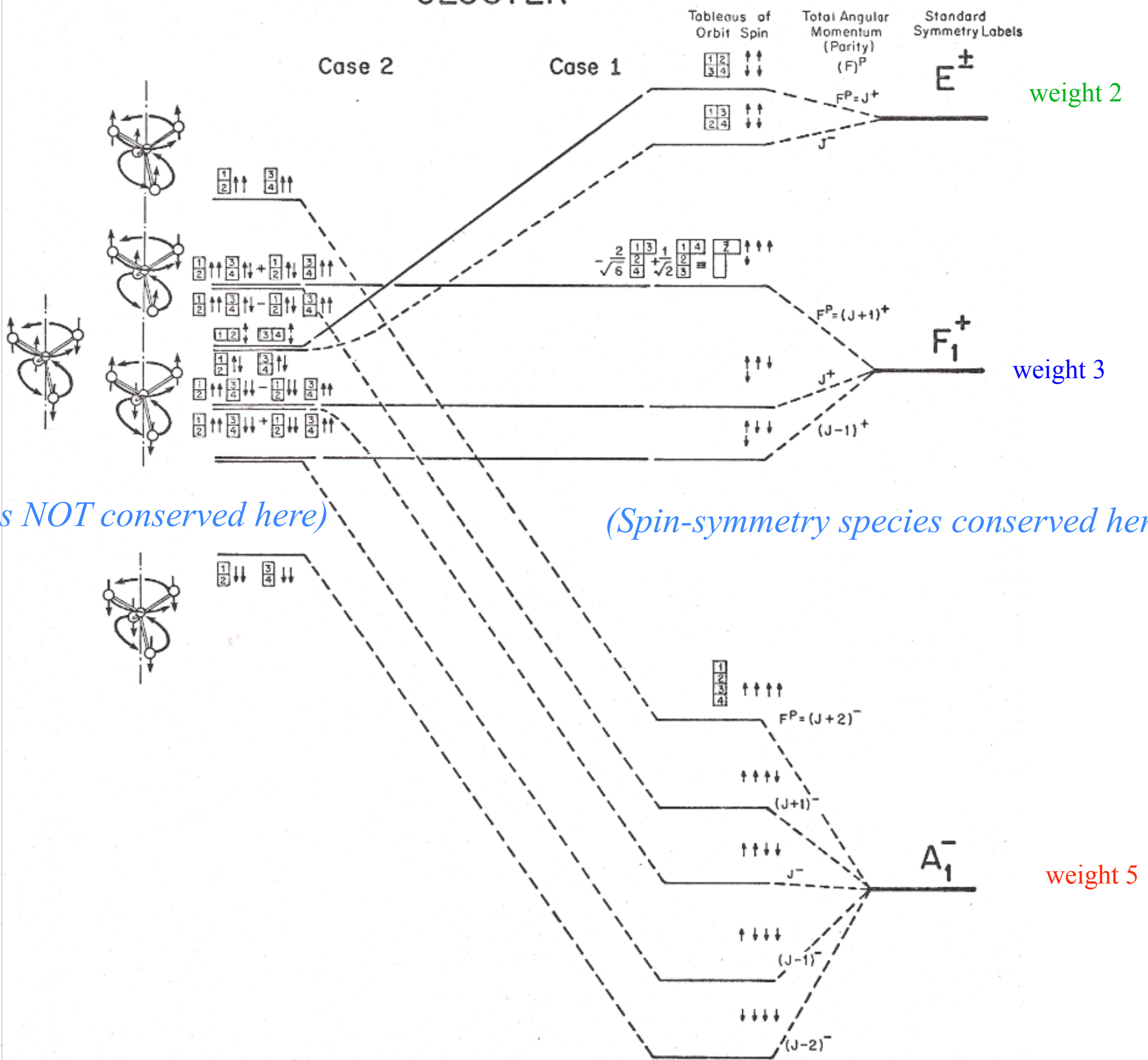
Transitions forbidden between states of different Bare Rotor quantum labels (Spin-symmetry species conserved here)



Present Complete T_d Labeling

			7^+ 7^-	7^+	7^-
			7^-	7^+	
			7^-	7^+	7^-
			7^+	7^-	7^+
			7^-	7^+	7^-
	$B = A_1$	A_2	E	F_1	F_2
CD ₄	$\frac{3 \cdot 4 \cdot 5 \cdot 6}{4 \cdot 3 \cdot 2 \cdot 1} = 15$	$\frac{3}{1} / \frac{4}{2} = 0$	$\frac{3 \cdot 4}{3 \cdot 2} = 6$	$\frac{3 \cdot 4}{2 \cdot 1} = 3$	$\frac{3 \cdot 4 \cdot 5}{4 \cdot 2 \cdot 1} = 15$
CH ₄	$\frac{2}{0} / \frac{4}{2} = 0$	$\frac{2 \cdot 3 \cdot 4 \cdot 5}{4 \cdot 3 \cdot 2 \cdot 1} = 5$	$\frac{2 \cdot 3}{3 \cdot 2} = 1$	$\frac{2 \cdot 3 \cdot 4}{4 \cdot 2 \cdot 1} = 3$	$\frac{2 \cdot 3}{0} / \frac{4}{2} = 0$
Statistical Weight Calculations					

$O_4 \uparrow 0$
CLUSTER



(Spin-symmetry species NOT conserved here)

(Spin-symmetry species conserved here)

Example of frequency hierarchy for $16\mu\text{m}$ spectra of CF_4 (Freon-14)

W.G.Harter

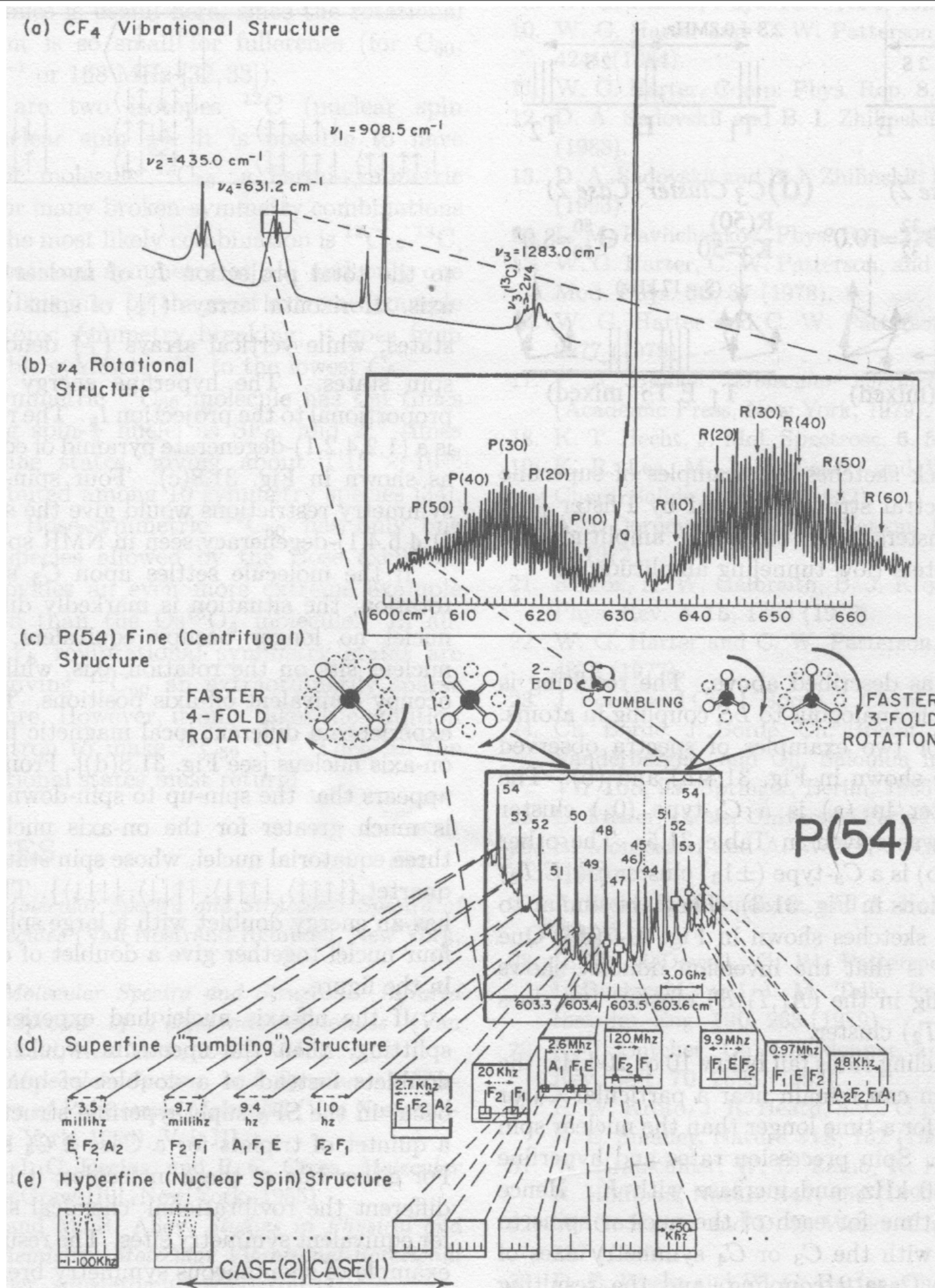
Ch. 31

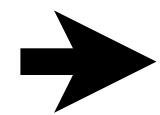
Atomic, Molecular, & Optical Physics Handbook

Am. Int. of Physics

Gordon Drake Editor

(1996)





S₆ and spin-symmetry for XY₆ molecules

Entanglement and Disentanglement

Resulting hyperfine spectra

Superhyperfine spectra

Spin-0 nuclei give Bose Exclusion

Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

boils down to :

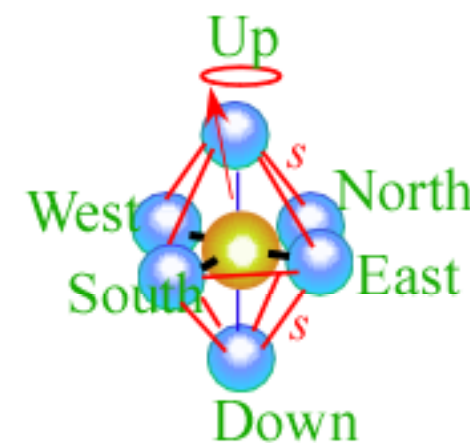
OUTSIDE versus INSIDE

Example:

*Cubic-Octahedral O
reduced to
Tetragonal C₄*

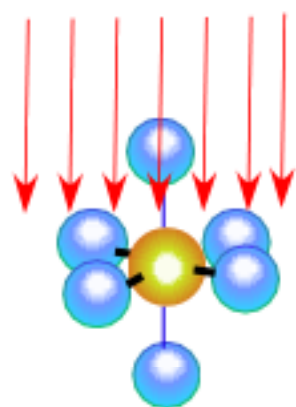
	<i>C₄</i>	<i>0₄</i>	<i>1₄</i>	<i>2₄</i>	<i>3₄</i>
<i>A₁</i>		1	.	.	.
<i>A₂</i>		.	.	1	.
<i>E</i>		1.	.	1	.
<i>T₁</i>		1	1	.	1
<i>T₂</i>		.	1	1	1

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



	<i> U></i>	<i> D></i>	<i> E></i>	<i> W></i>	<i> N></i>	<i> S></i>
<i>H</i>	0	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>0</i>	<i>H</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	<i>H</i>	0	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	0	<i>H</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>H</i>	0	<i>s</i>
<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	0	<i>H</i>	<i>s</i>

*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")*

Review O ⊃ C₄ correlations:

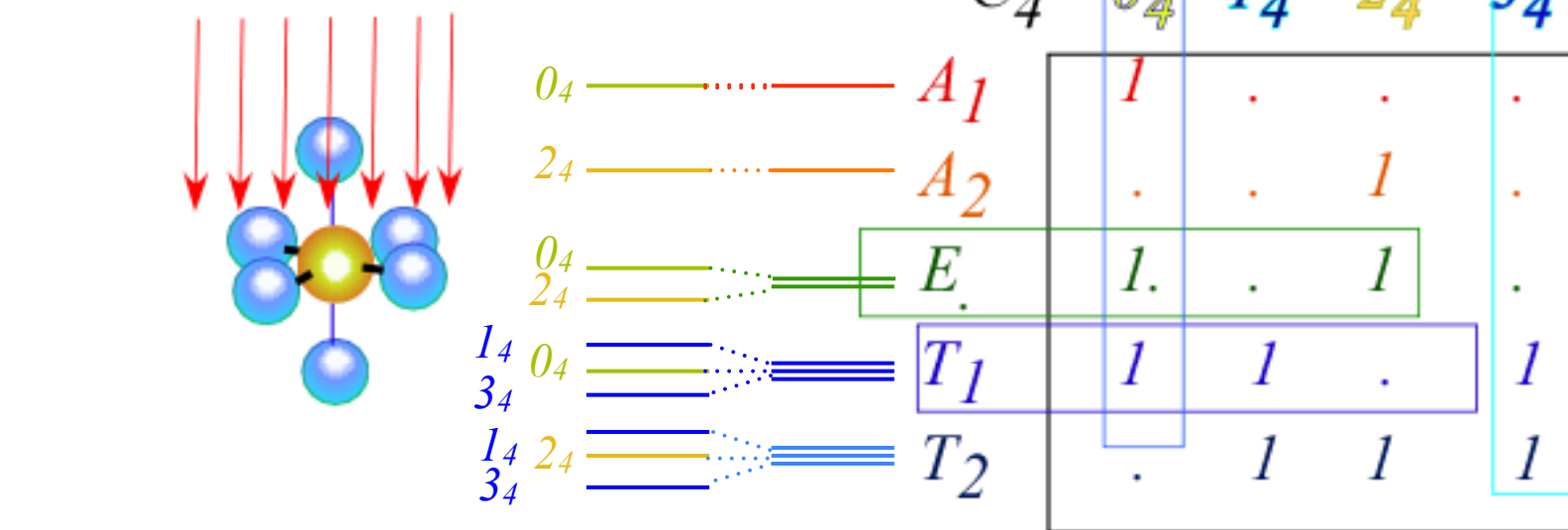
Duality: The "Flip Side" of Symmetry Analysis.

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

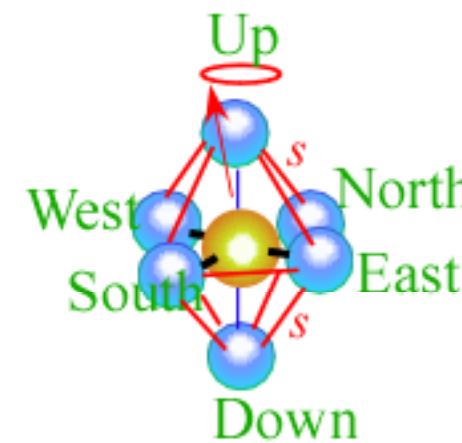
LAB versus BODY, **STATE versus PARTICLE,**
boils down to :
OUTSIDE versus INSIDE

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

Example:
Cubic-Octahedral *O*
reduced to
Tetragonal *C₄*



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



	U>	D>	E>	W>	N>	S>
<i>H</i>	0	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
0	<i>H</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	<i>H</i>	0	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	0	<i>H</i>	<i>s</i>	<i>s</i>	<i>s</i>
<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	<i>H</i>	0	<i>s</i>
<i>s</i>	<i>s</i>	<i>s</i>	<i>s</i>	0	<i>H</i>	<i>s</i>

Review *O* ⊃ *C₄* correlations:

Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

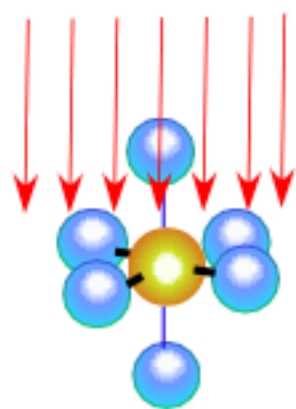
boils down to :

OUTSIDE versus INSIDE

OUTSIDE or LAB
Symmetry reduction
results in

Level or Spectral
SPLITTING

External B-field
does Zeeman splitting



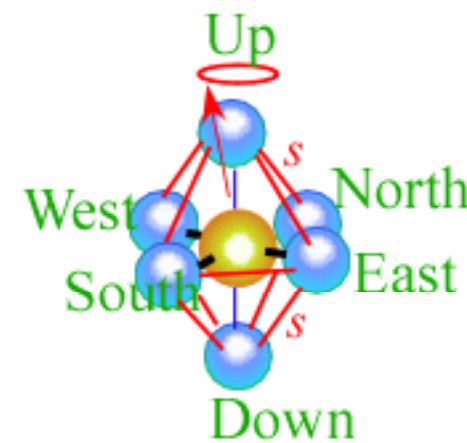
INSIDE or BODY
Symmetry reduction
results in

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

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



	$ U\rangle$	$ D\rangle$	$ E\rangle$	$ W\rangle$	$ N\rangle$	$ S\rangle$
H	0	s	s	s	s	s
0	H	s	s	s	s	s
s	s	H	0	s	s	s
s	s	0	H	s	s	s
s	s	s	s	H	0	s
s	s	s	s	0	H	s

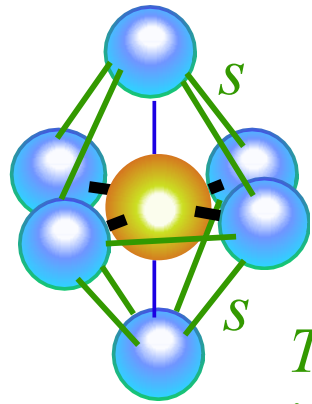
Review $O \supset C_4$ correlations:



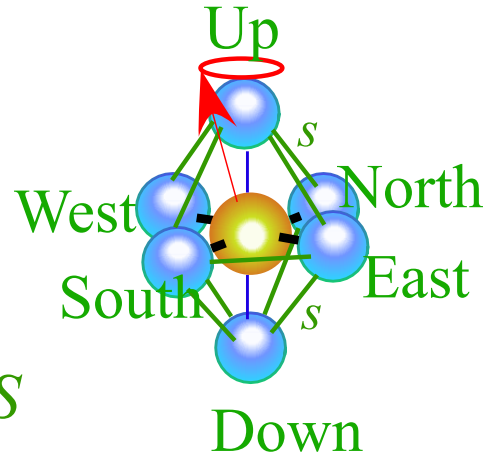
Tunneling (s) between axes
splits the 0_4 cluster as
shown on following pages

0_4 cluster splitting (derived on following page)

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



Tunneling $s=-S$
is negative here



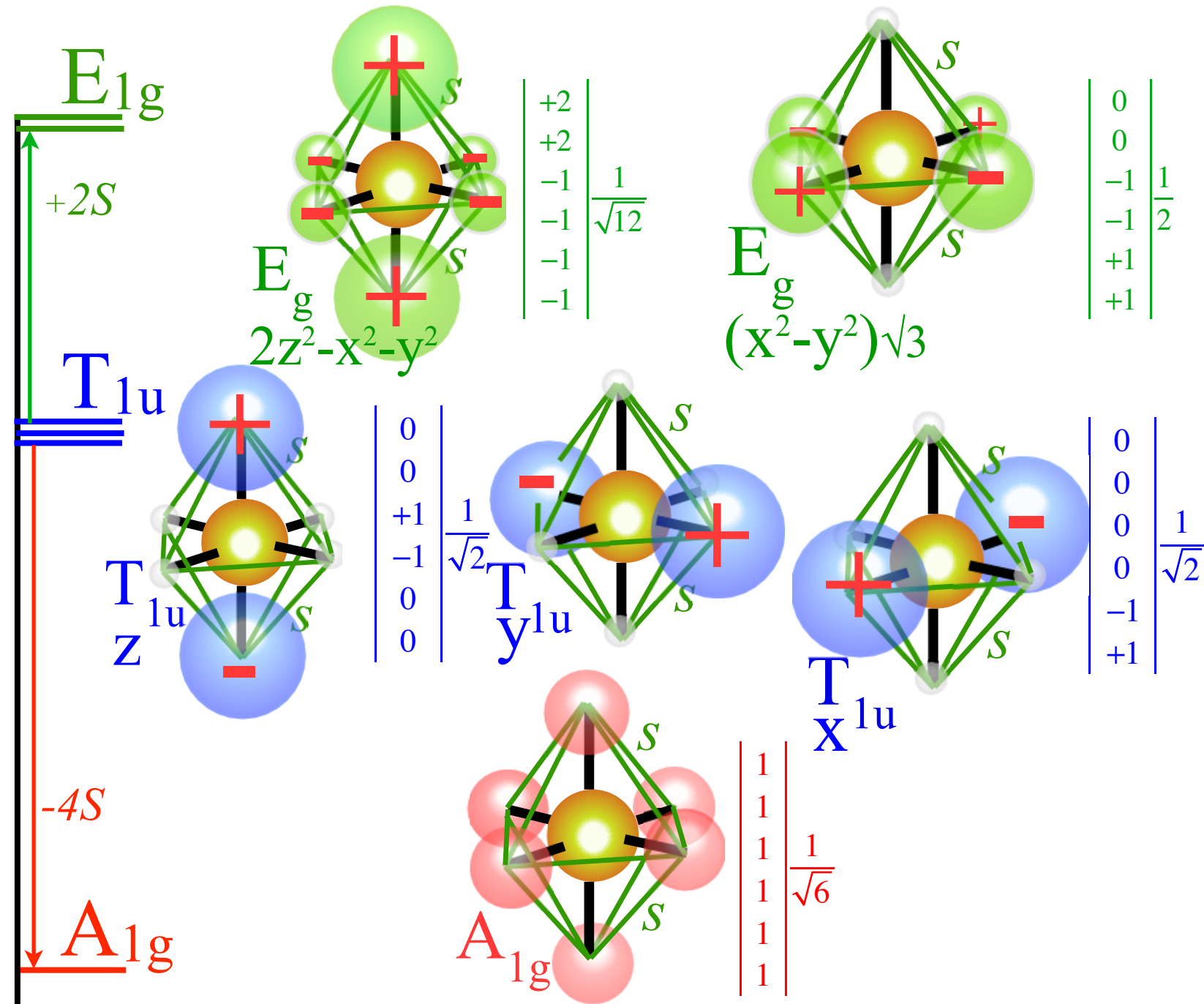
	$ U\rangle$	$ D\rangle$	$ E\rangle$	$ W\rangle$	$ N\rangle$	$ S\rangle$
H	0	s	s	s	s	s
0	H	s	s	s	s	s
s	s	H	0	s	s	s
s	s	0	H	s	s	s
s	s	s	s	H	0	s
s	s	s	s	0	H	s

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

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

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

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



Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

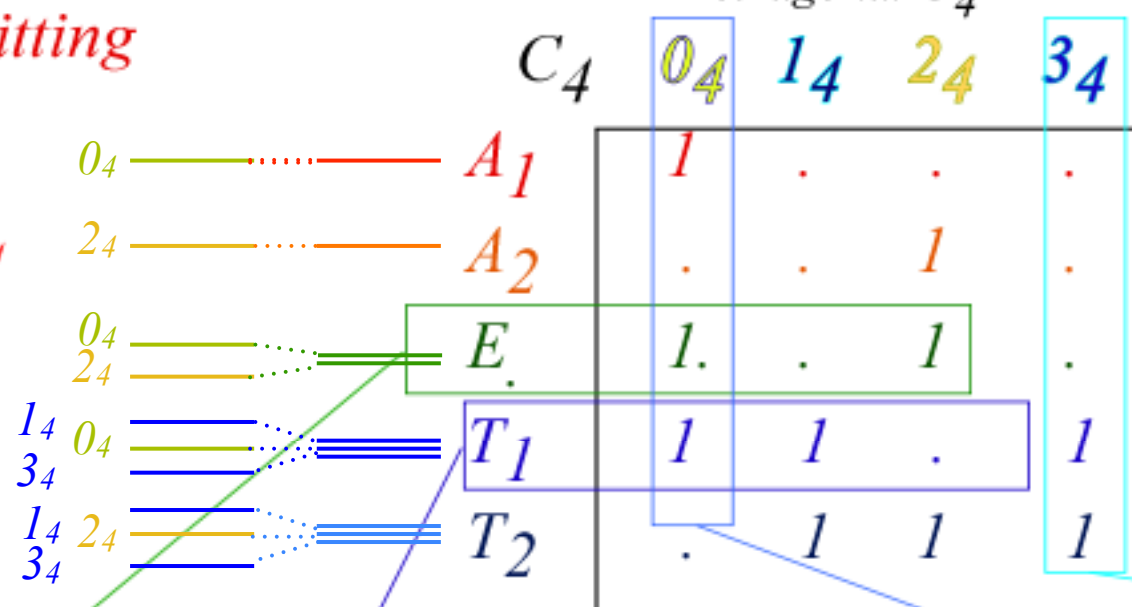
boils down to :

OUTSIDE versus INSIDE

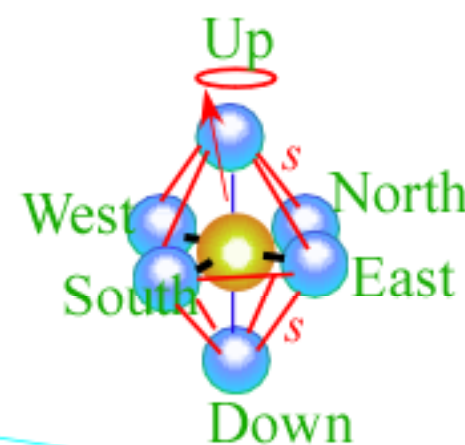
OUTSIDE or LAB
Symmetry reduction
results in
Level or Spectral
SPLITTING
External B-field
does Zeeman splitting

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

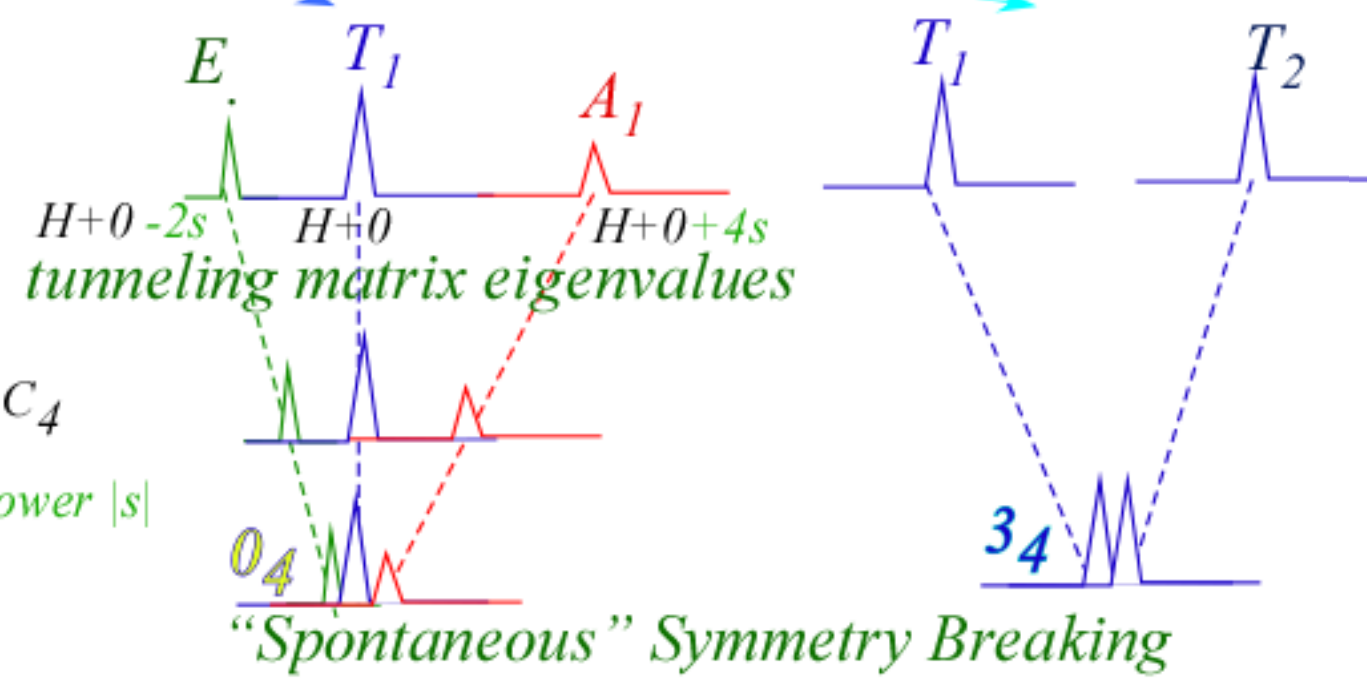
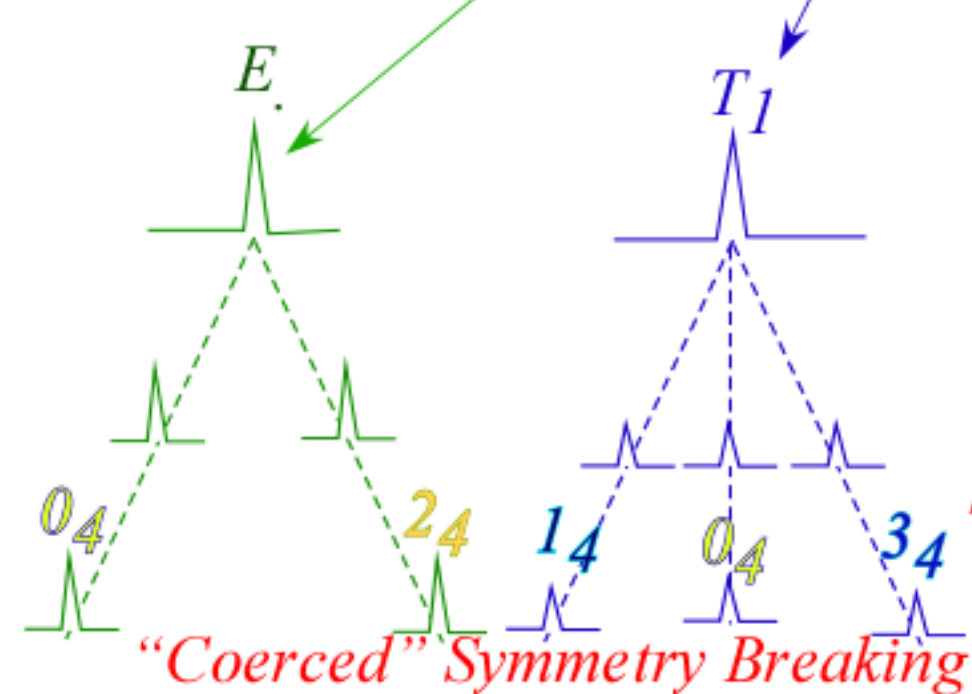
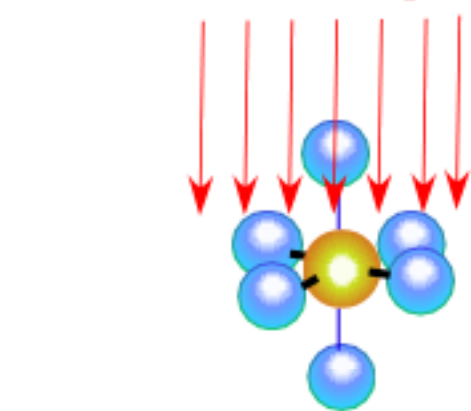
Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4



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




	$ U\rangle$	$ D\rangle$	$ E\rangle$	$ W\rangle$	$ N\rangle$	$ S\rangle$
H	0	s	s	s	s	s
0	H	s	s	s	s	s
s	s	H	0	s	s	s
s	s	0	H	s	s	s
s	s	s	s	H	0	s
s	s	s	s	0	H	s



Stronger C_4
higher $|B|$ lower $|s|$

tunneling matrix eigenvalues
 $H+0-2s$ $H+0$ $H+0+4s$



S₆ and spin-symmetry for XY₆ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion

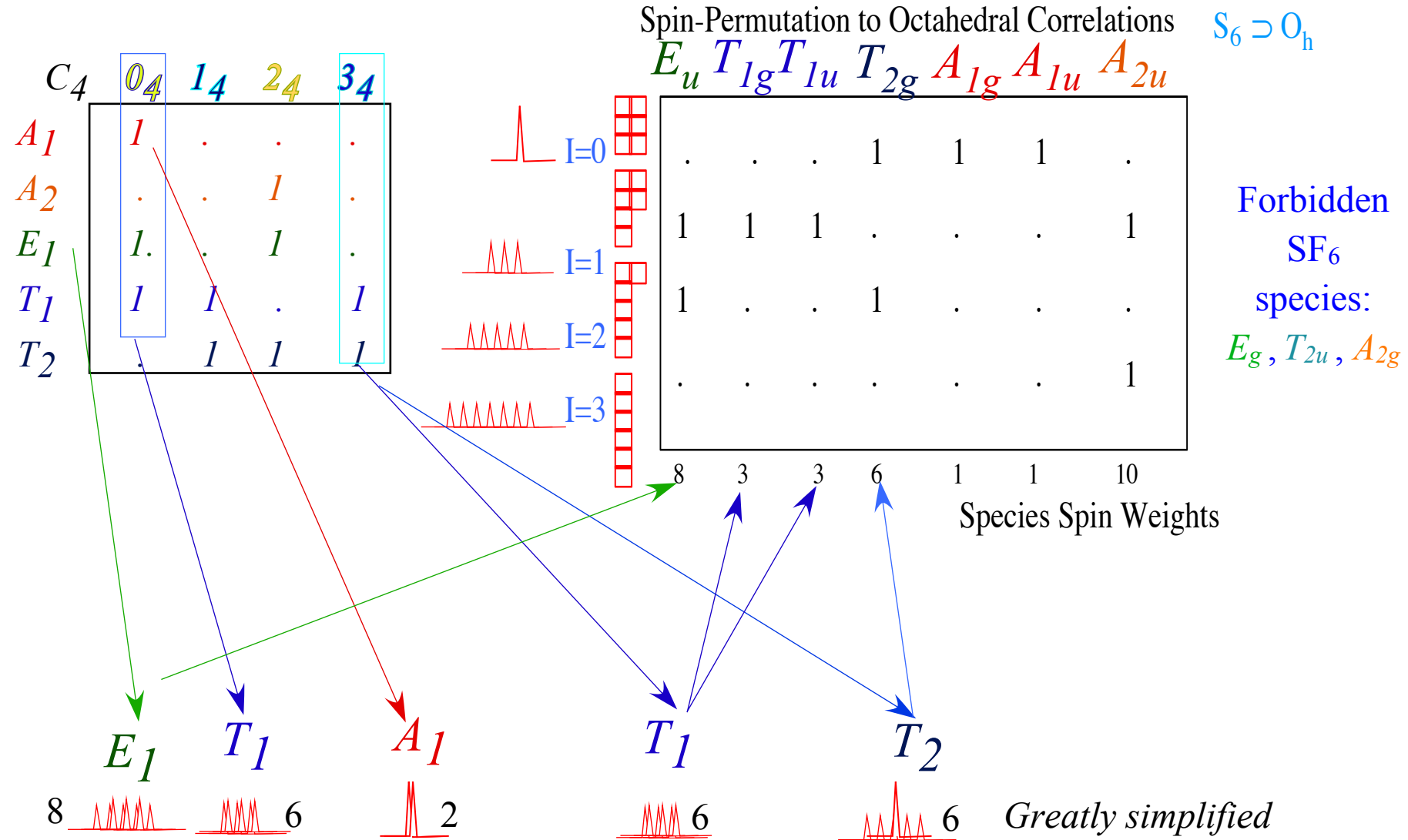
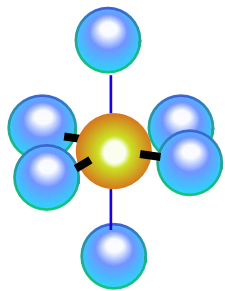
Entanglement!

How F-nuclei become entangled

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

With rotation

all six  nuclei are equivalent

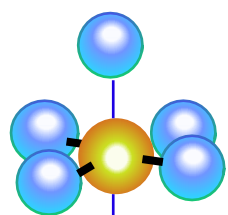


Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde', C. Saloman, and Oliver Pfister (Pfister did SiF_4 , too.)

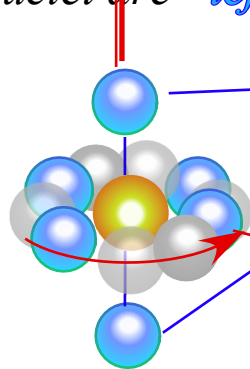
DISentanglement!

How F-nuclei become distinguished (but not distinguishable) in SF₆.

Without rotation being stuck on C₄ axis all six nuclei are equivalent



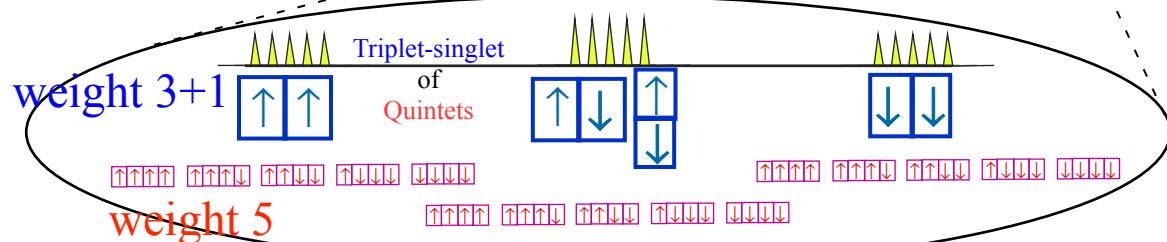
With rotation stuck on C₄ axis polar nuclei are "left out in the cold"



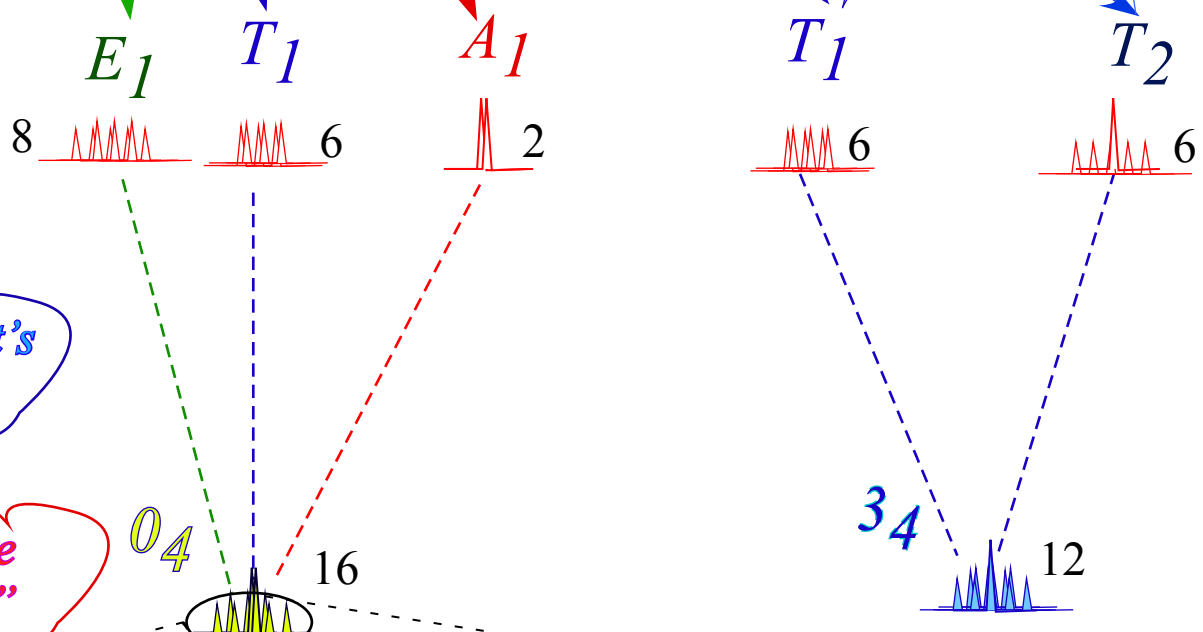
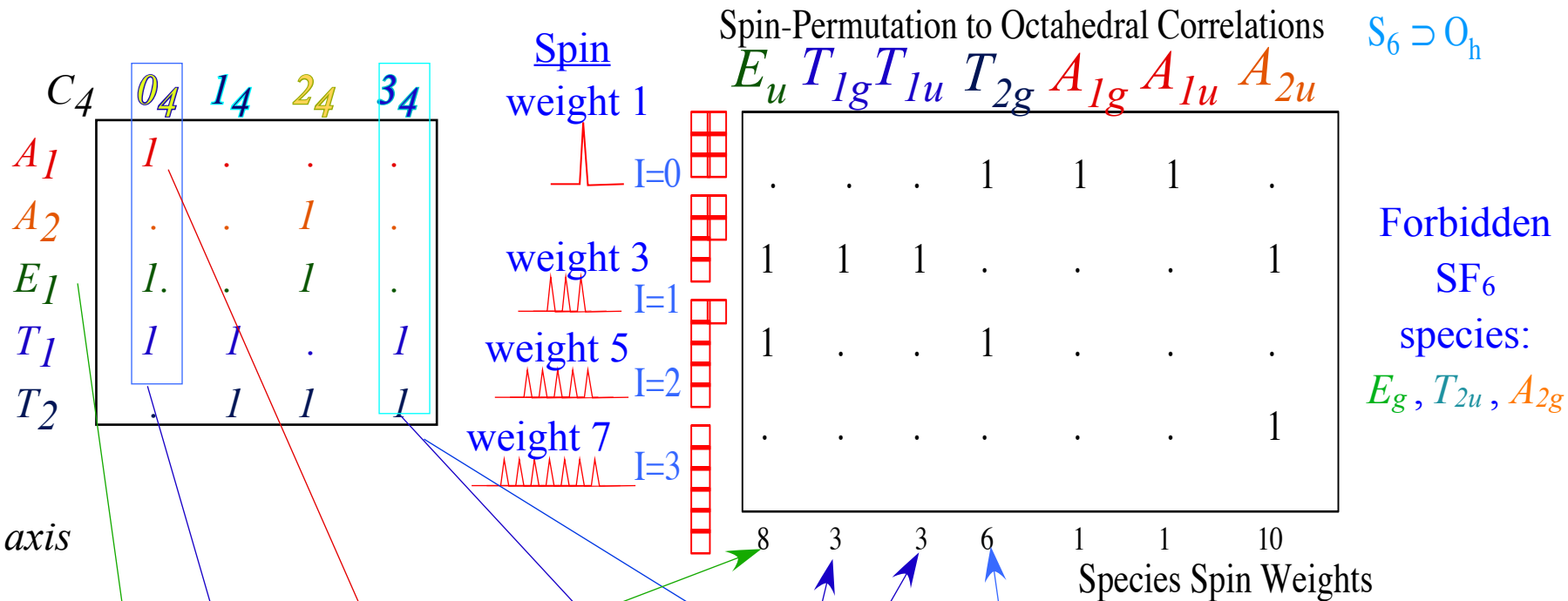
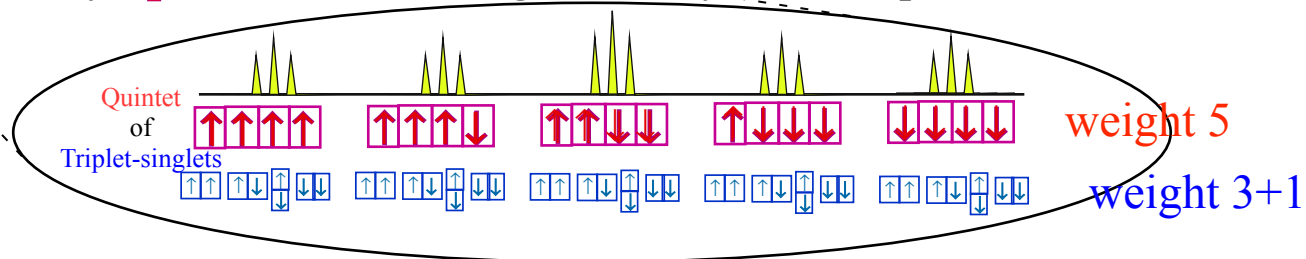
"Brrr-rr it's cold!"

"WE like it HOT!"

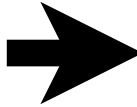
If polar nuclei in greater B-field than equatorial-nuclei...

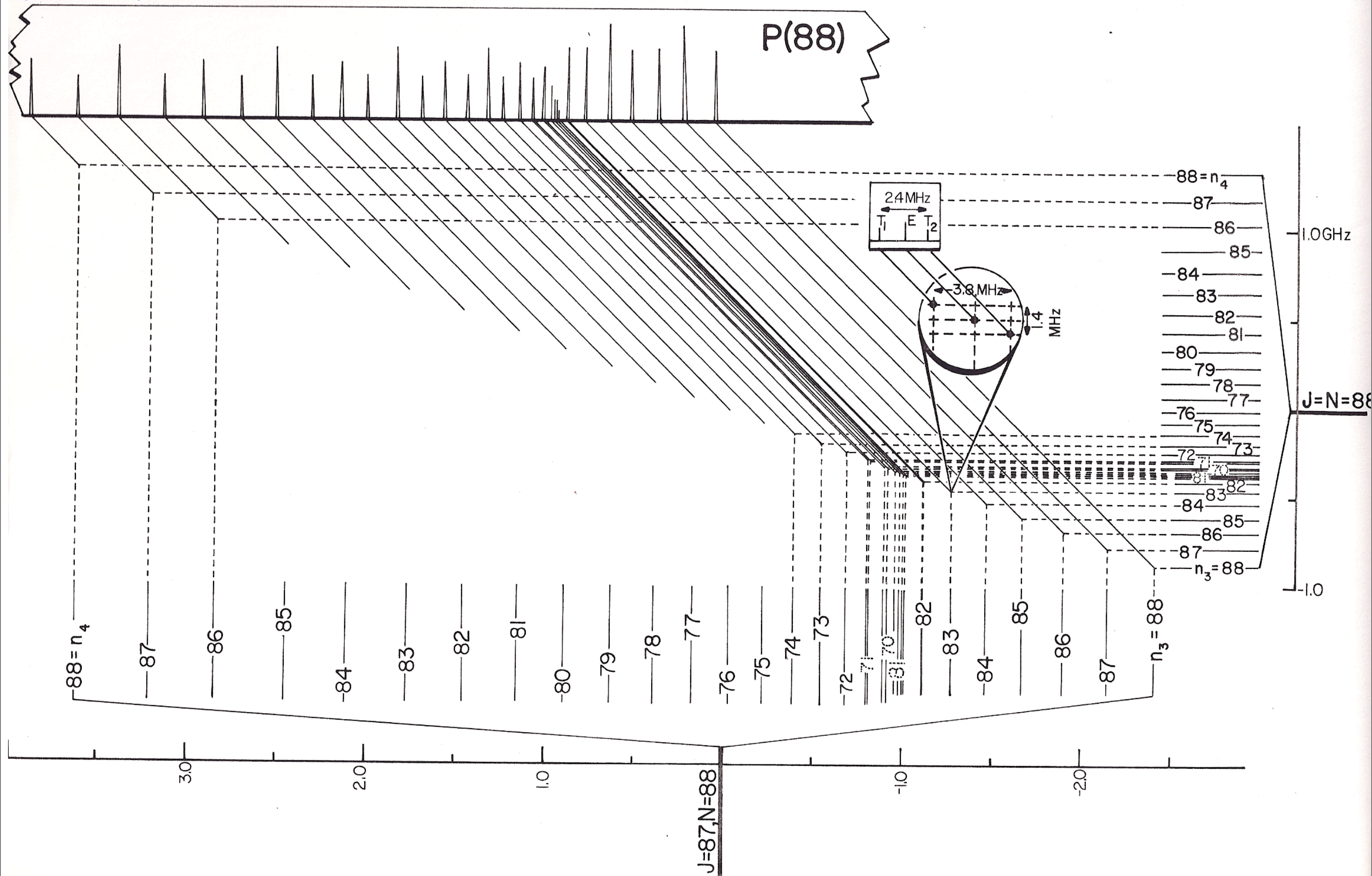


If equatorial nuclei in greater B-field than polar-nuclei...



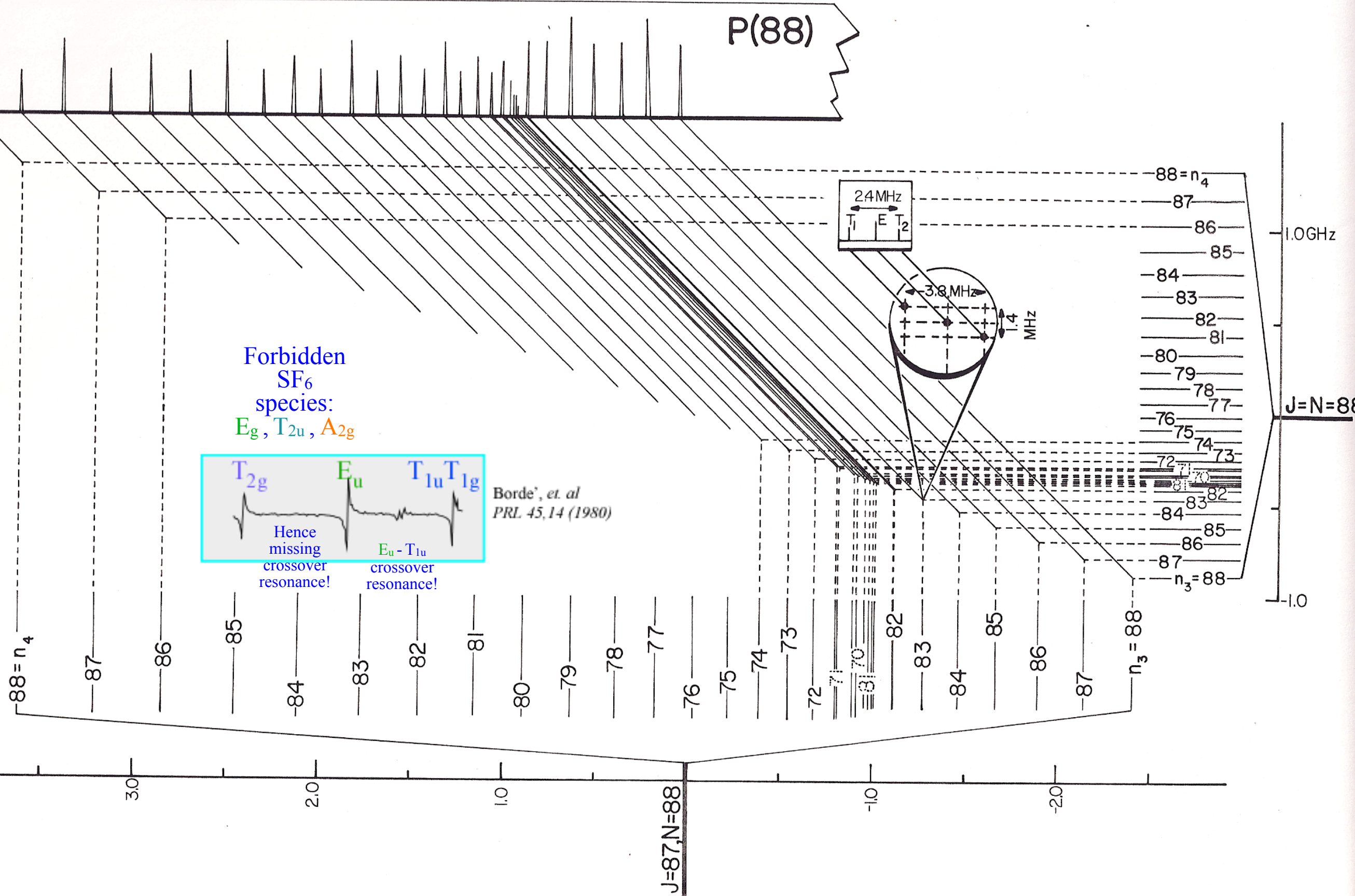
Greatly simplified sketches of ultra high resolution IR SF₆ spectroscopy of Christian Borde', C. Saloman, and Oliver Pfister (Pfister did SiF₄, too.)

S₆ and spin-symmetry for XY₆ molecules
Entanglement and Disentanglement
 *Resulting hyperfine spectra*
Superhyperfine spectra
Spin-0 nuclei give Bose Exclusion

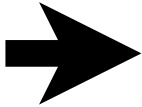


Harter, Phys. Rev. A 24, 192-263 (1981)

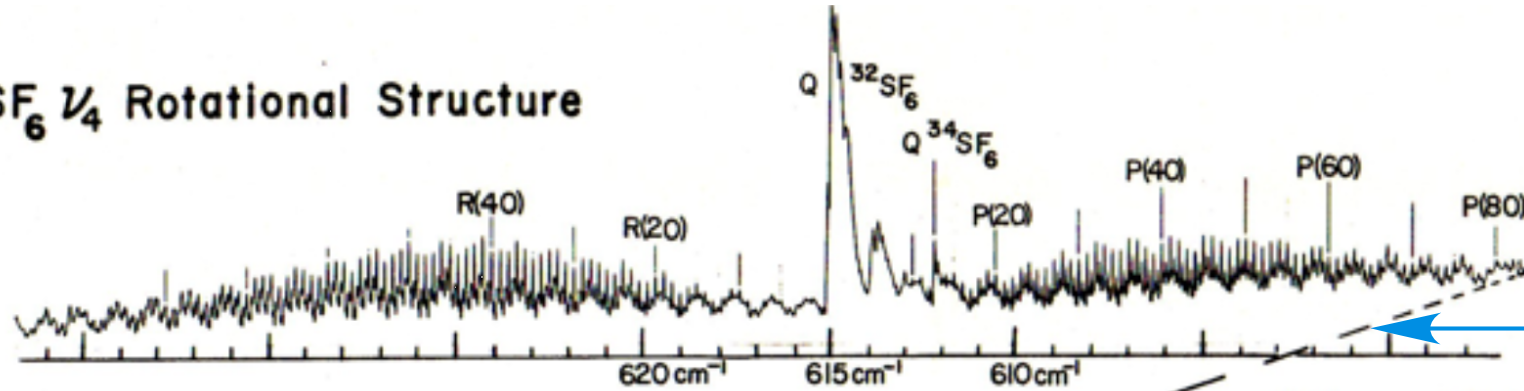
Example of subtle parity effect in SF₆ superfine-hyperfine transitions



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

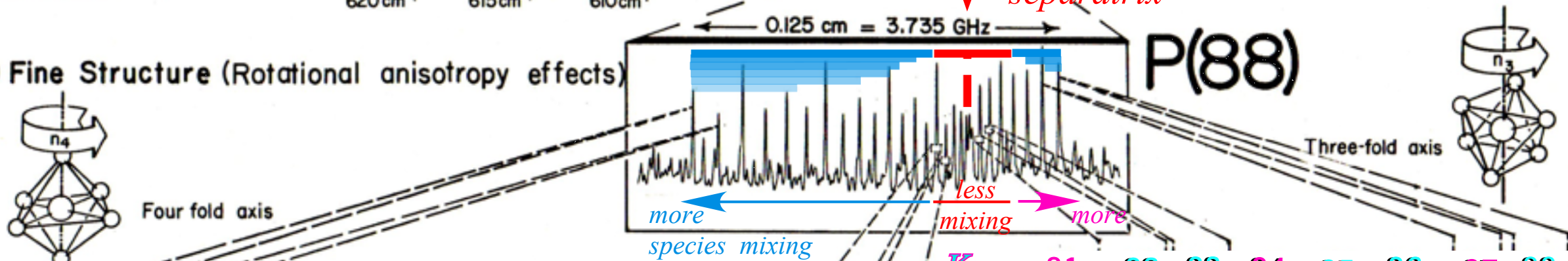
S₆ and spin-symmetry for XY₆ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
 *Superhyperfine spectra*
Spin-0 nuclei give Bose Exclusion

(a) SF₆ 1/4 Rotational Structure

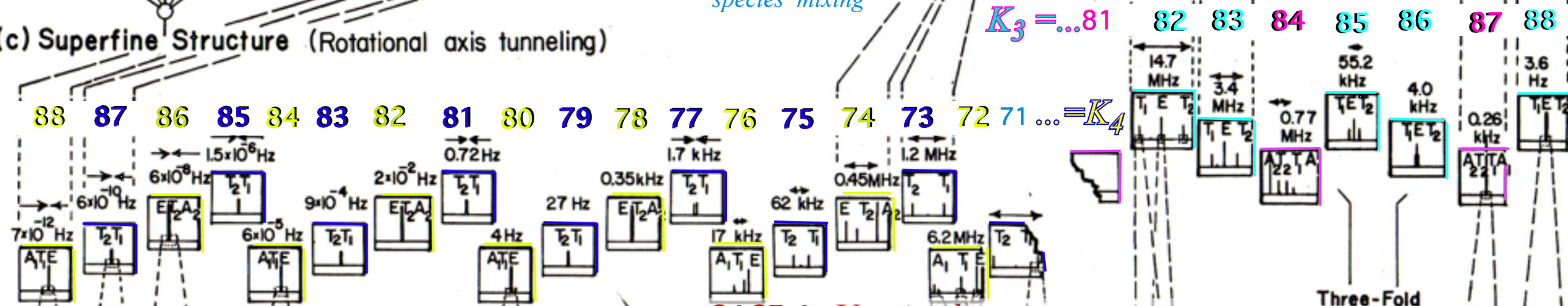


Primary AET species mixing increases with distance from "separatrix"

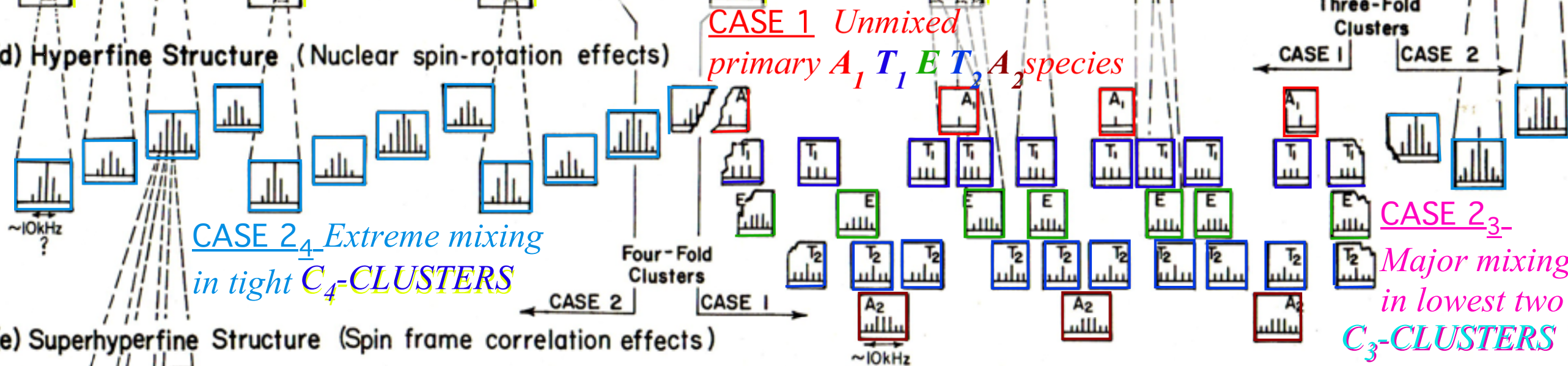
(b) P(88) Fine Structure (Rotational anisotropy effects)



(c) Superfine Structure (Rotational axis tunneling)



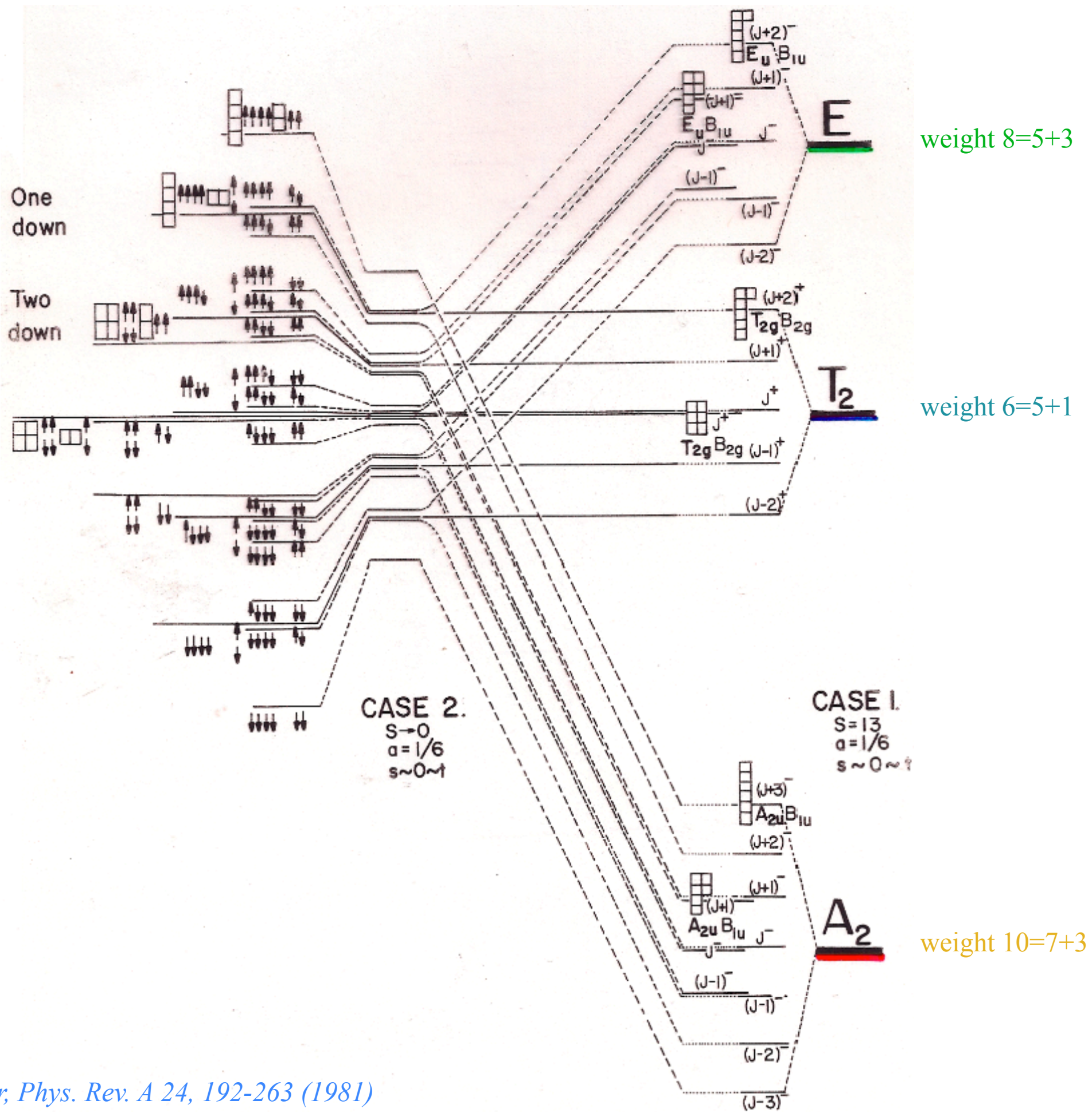
(d) Hyperfine Structure (Nuclear spin-rotation effects)



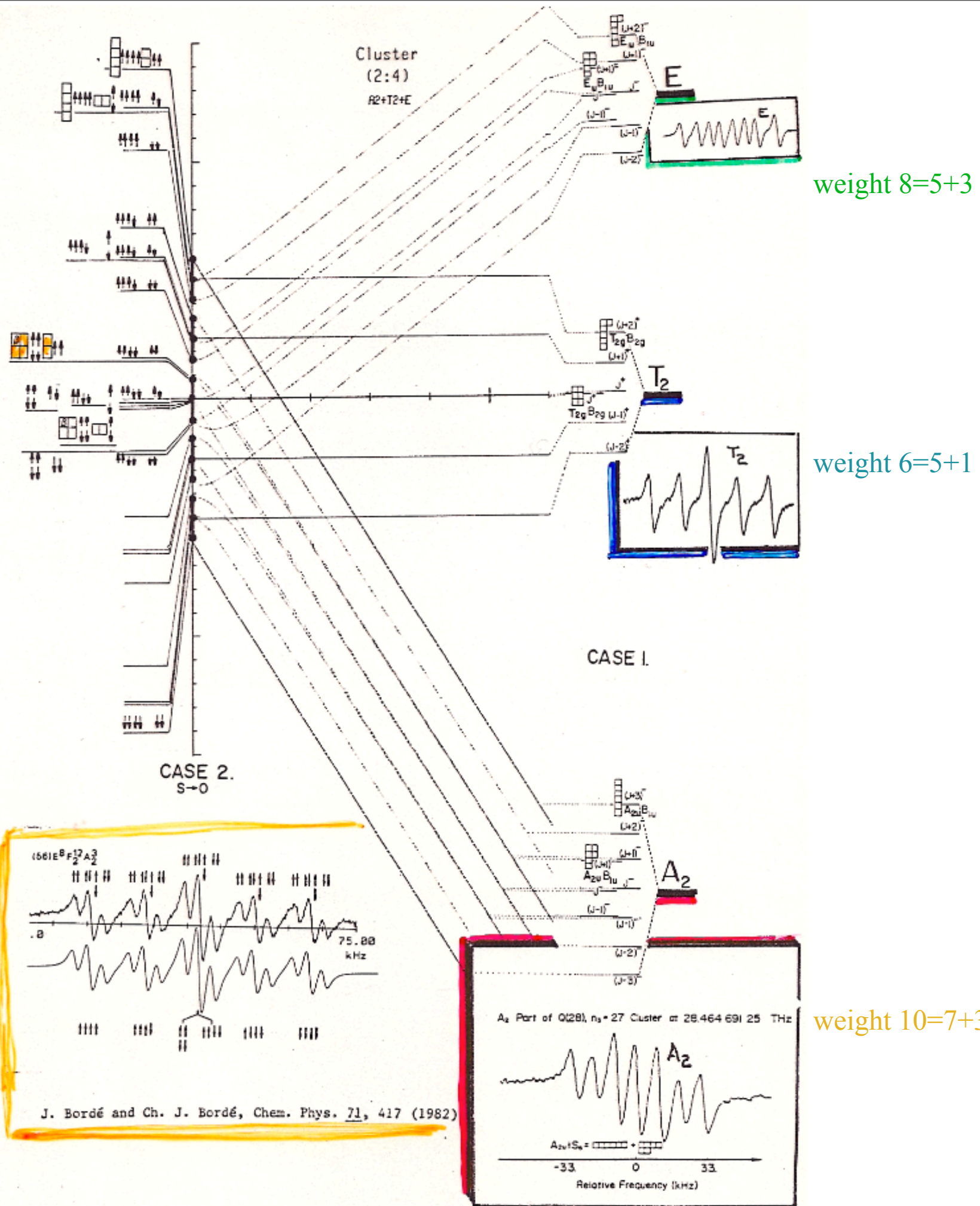
(e) Superhyperfine Structure (Spin frame correlation effects)

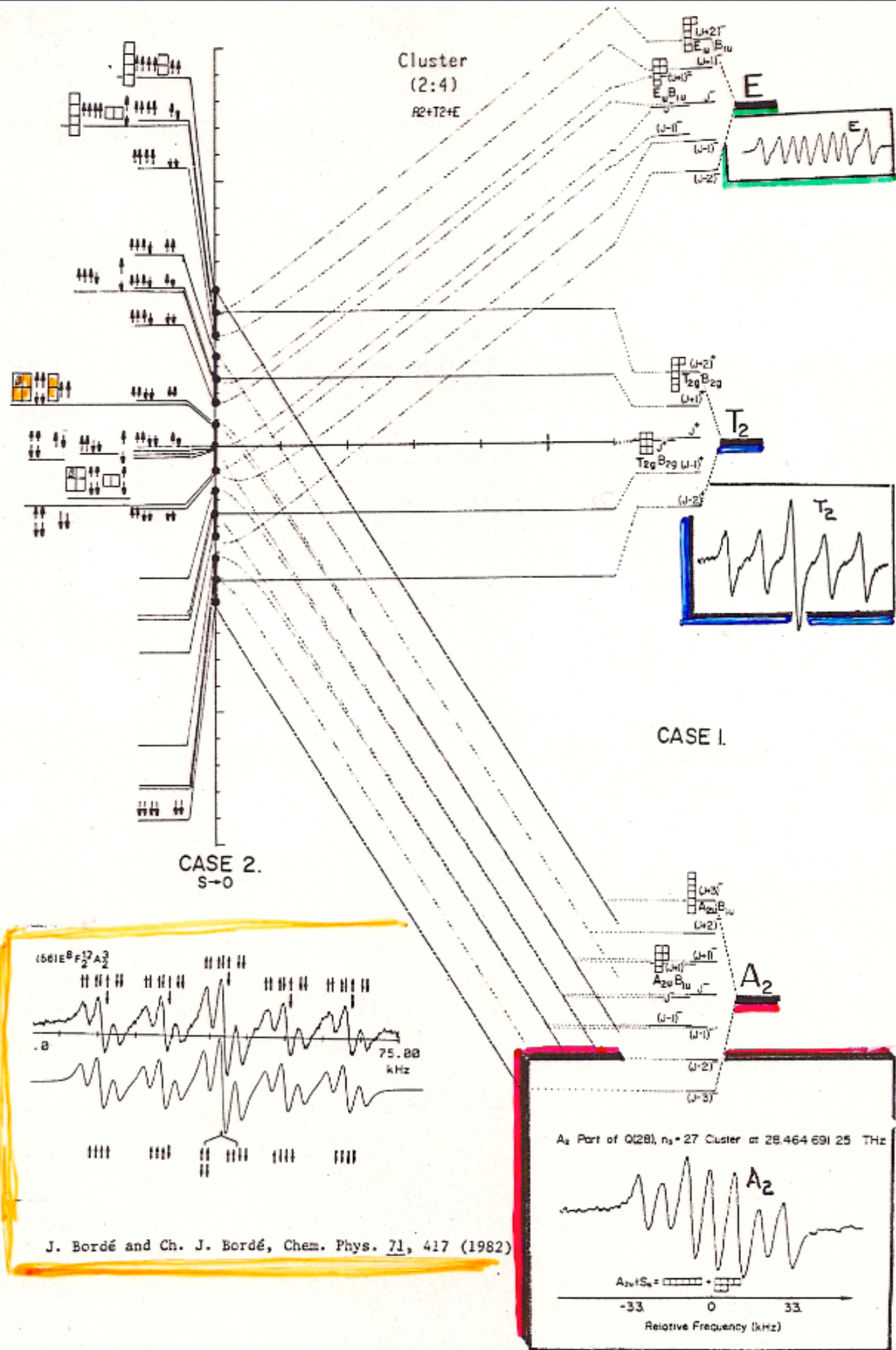


Harter, Phys. Rev. A 24, 192-263 (1981)

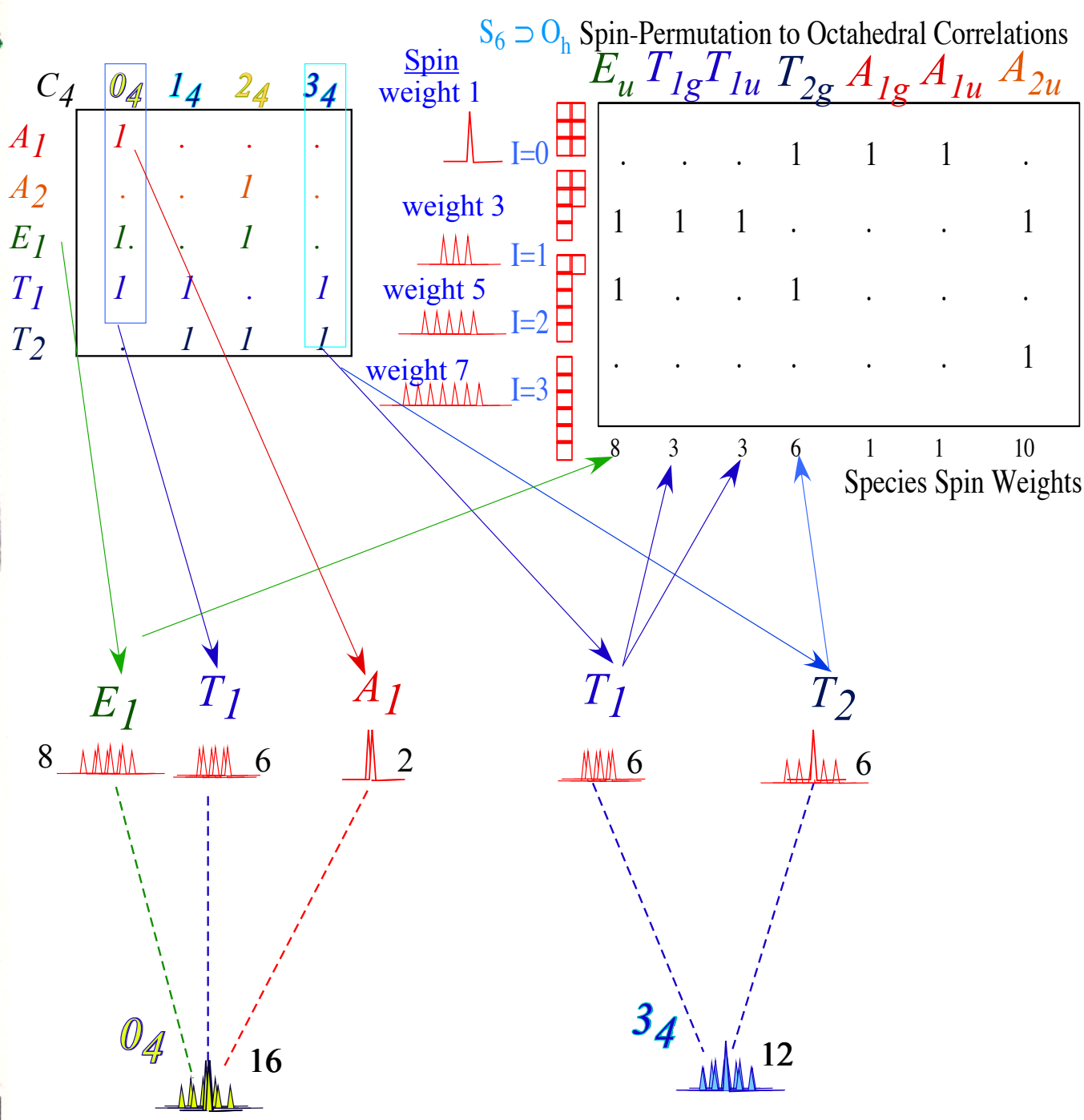



Harter, Phys. Rev. A 24, 192-263 (1981)





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

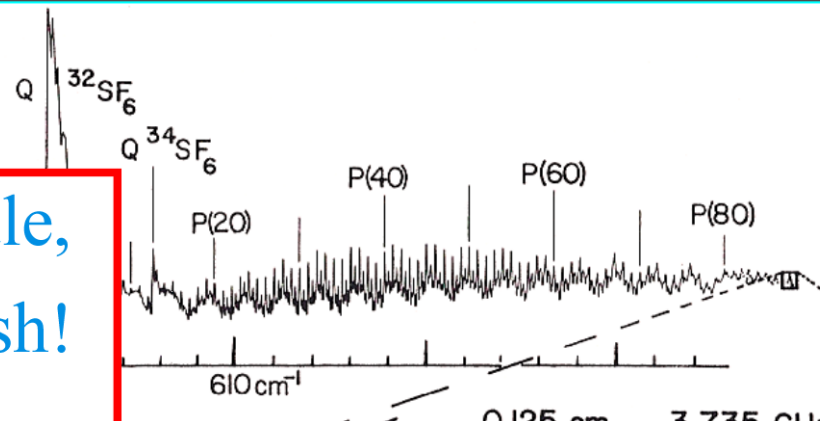


S₆ and spin-symmetry for XY₆ molecules
Entanglement and Disentanglement
Resulting hyperfine spectra
Superhyperfine spectra
 *Spin-0 nuclei give Bose Exclusion*

Spin-0 nuclei give Bose Exclusion

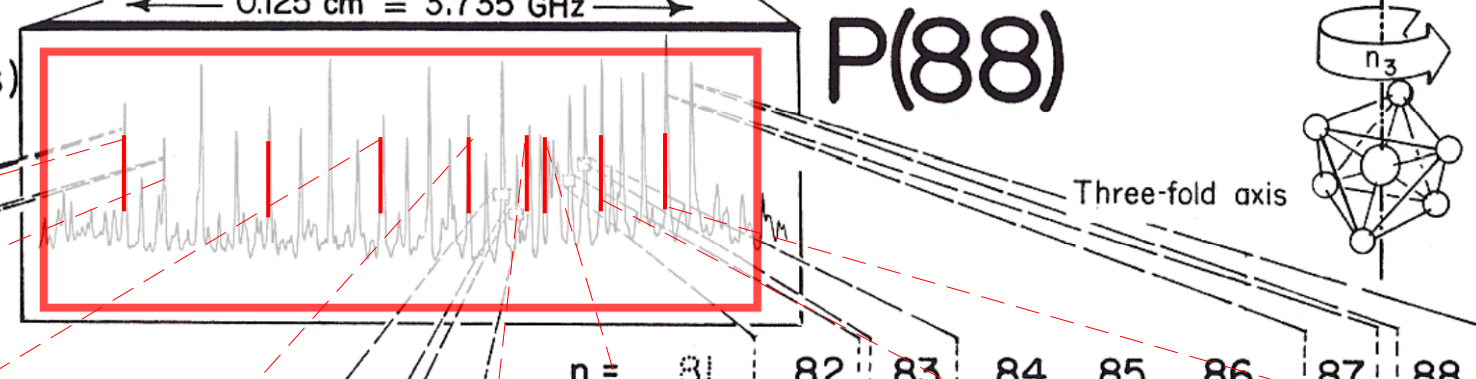
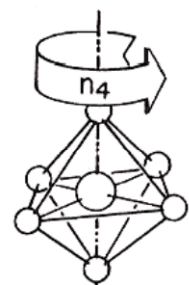
(a) SF₆ ν₄ Rotational Structure

For a zero-spin X¹⁶O₆ molecule, hundreds of lines would vanish! Just eight A₁ singlets remain.

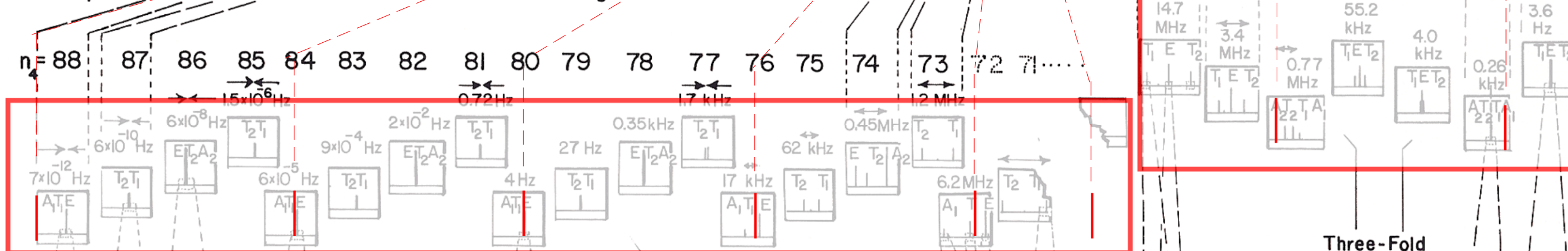


FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. **76**, 322 (1979).

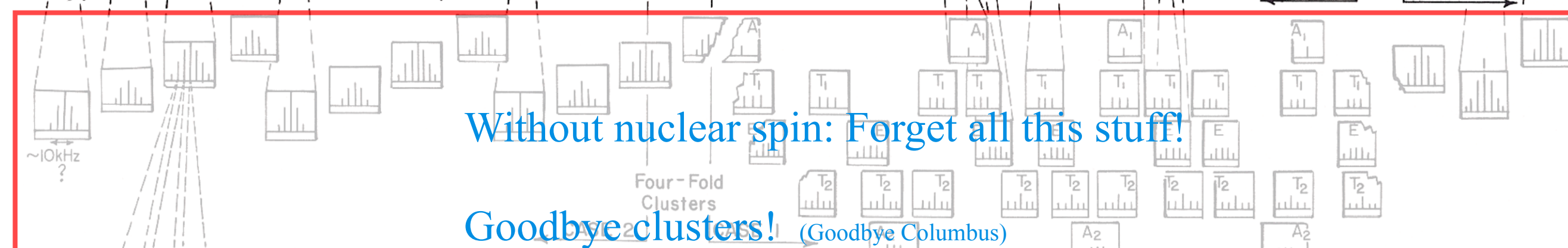
(b) P(88) Fine Structure (Rotational anisotropy effects)



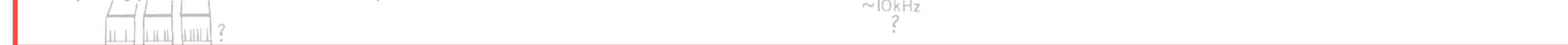
(c) Superfine Structure (Rotational axis tunneling)



(d) Hyperfine Structure (Nuclear spin-rotation effects)

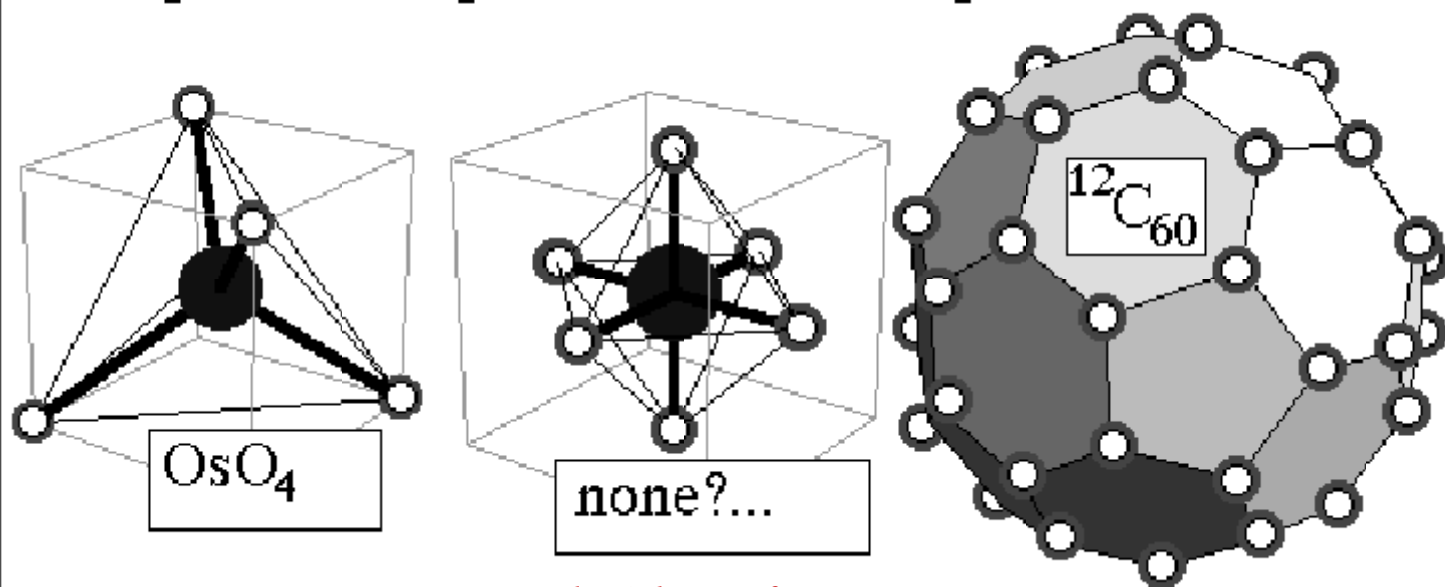


(e) Superhyperfine Structure (Spin frame correlation effects)



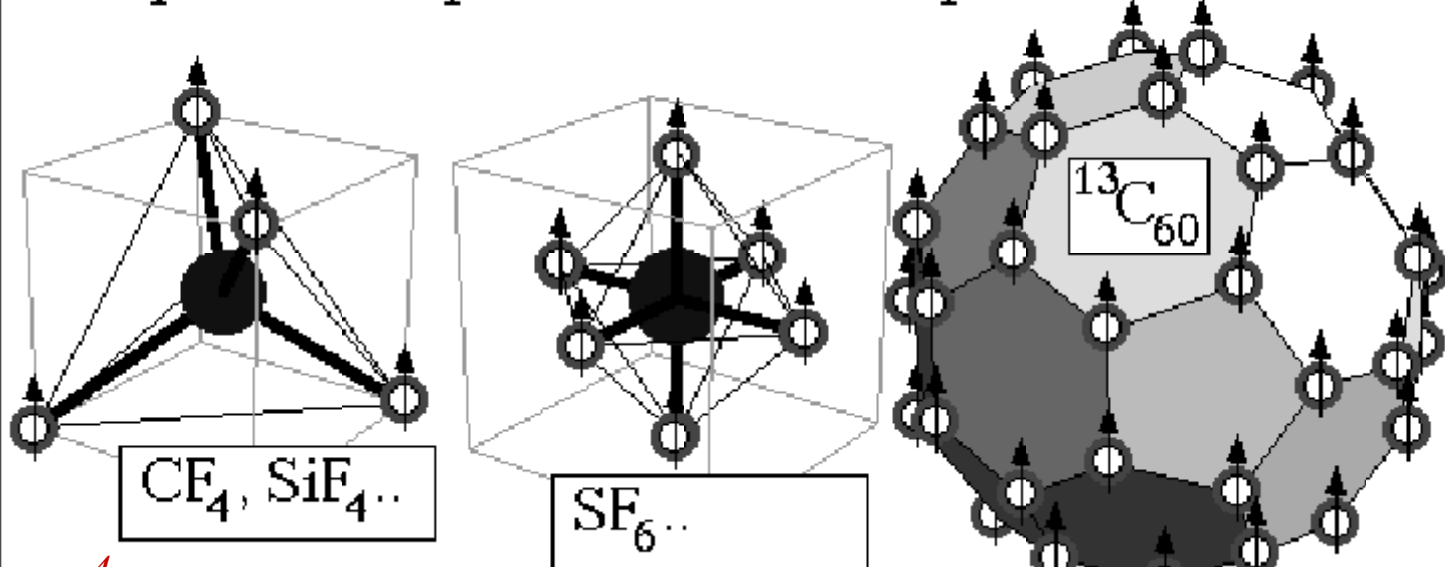
Some examples of Bose Exclusion

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: $I=0-2$

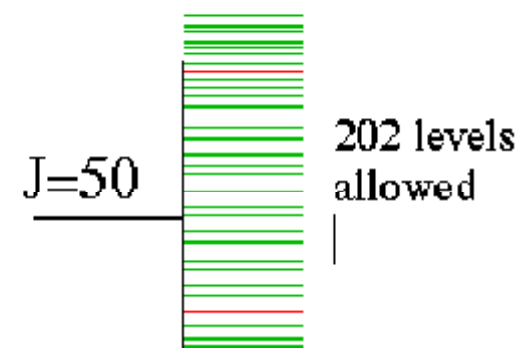
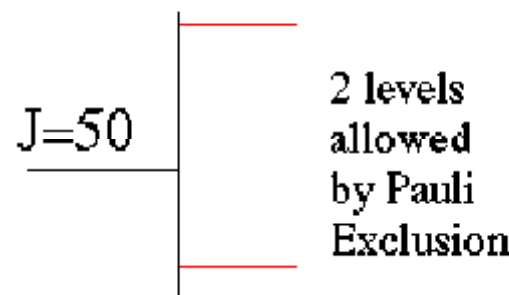
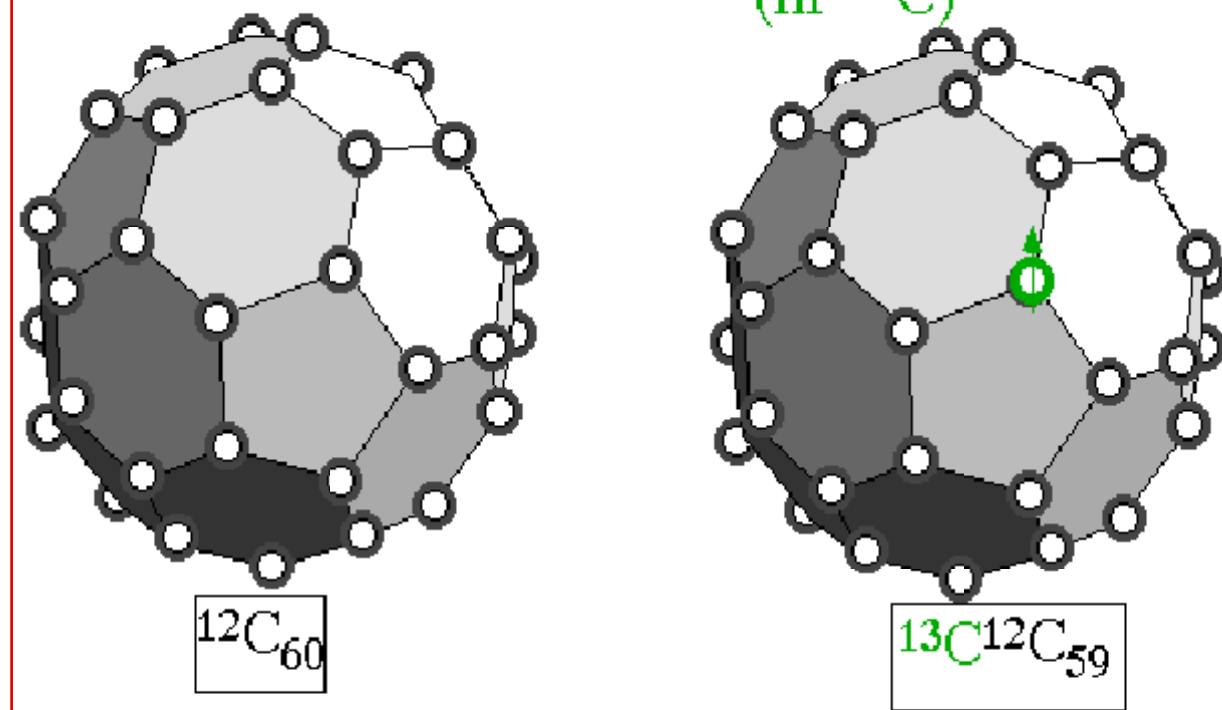
$2^6=64$ hyperfine states: $I=0-3$

$2^{60}=1.15 \times 10^{18}$ 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 ¹³C)



Question: Where did those 200 levels go?

Better Question: Where did those 1.15 octillion levels go?

Some examples of Fermi (non) Exclusion

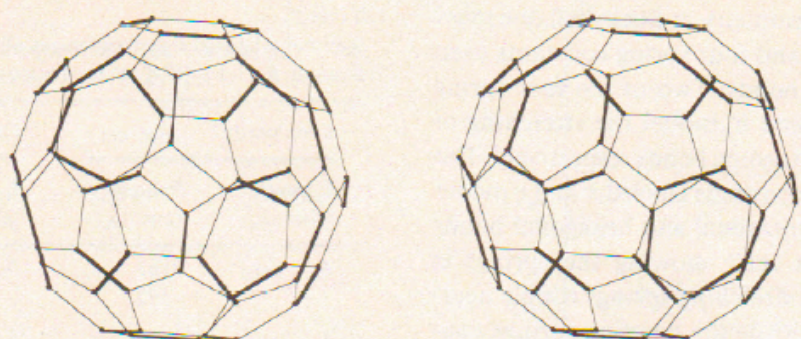


Fig. 1. Stereoscopic view of Buckyball. "Double bonds" lie along the darker lines and "single bonds" lie along the lighter lines. Carbon atoms are located at the vertices.

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

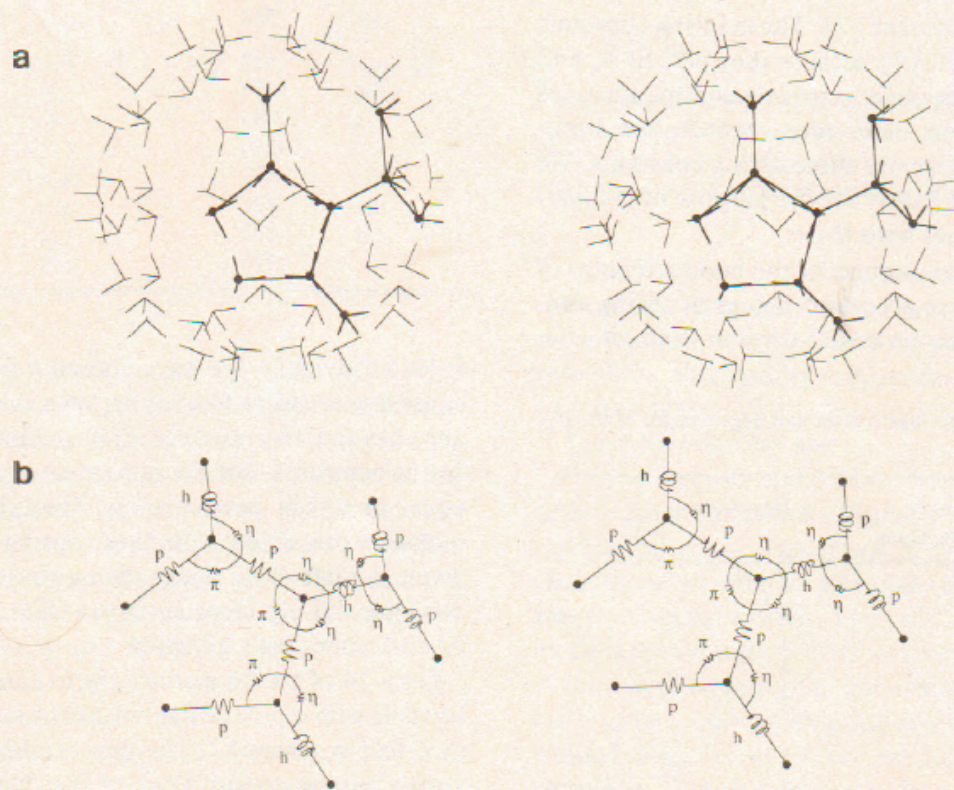


Fig. 2. (a) Stereoscopic view of the 60 orthogonal coordinate triads used in the initial formulation of the force matrix. The unit cell is highlighted. (b) Stereoscopic view of the unit cell required for the calculation of the force matrix. Single bond parameters are p and π . Double bond parameters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

Table 5
Symmetry-labeled eigenfrequencies of Buckyball for
 $p=h=7.6 \times 10^5$ dyn/cm, $\pi=\eta=0.7 \times 10^5$ 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_g	1662	T_{1u}	1868		
	1045		1462		
	513		618		
			478		
G_g	1900	T_{2u}	1954		
	951		1543		
	724		1122		
	615		526		
			358		
H_g	2006	G_u	2004		
	1813		1845		
	1327		1086		
	657		876		
	593		663		
	433		360		
	H_u		2068	H_u	2086
			1910		1797
1575		1464			
1292		849			
828		569			
526		470			
413		405			
274					

directions. 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

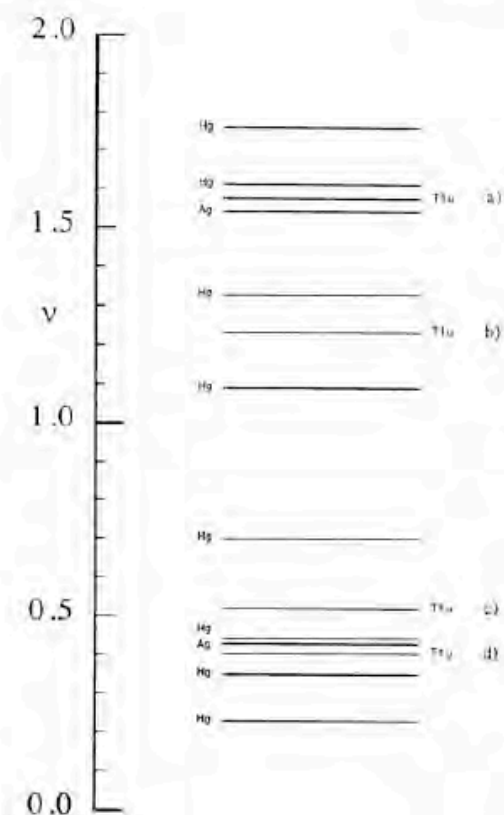


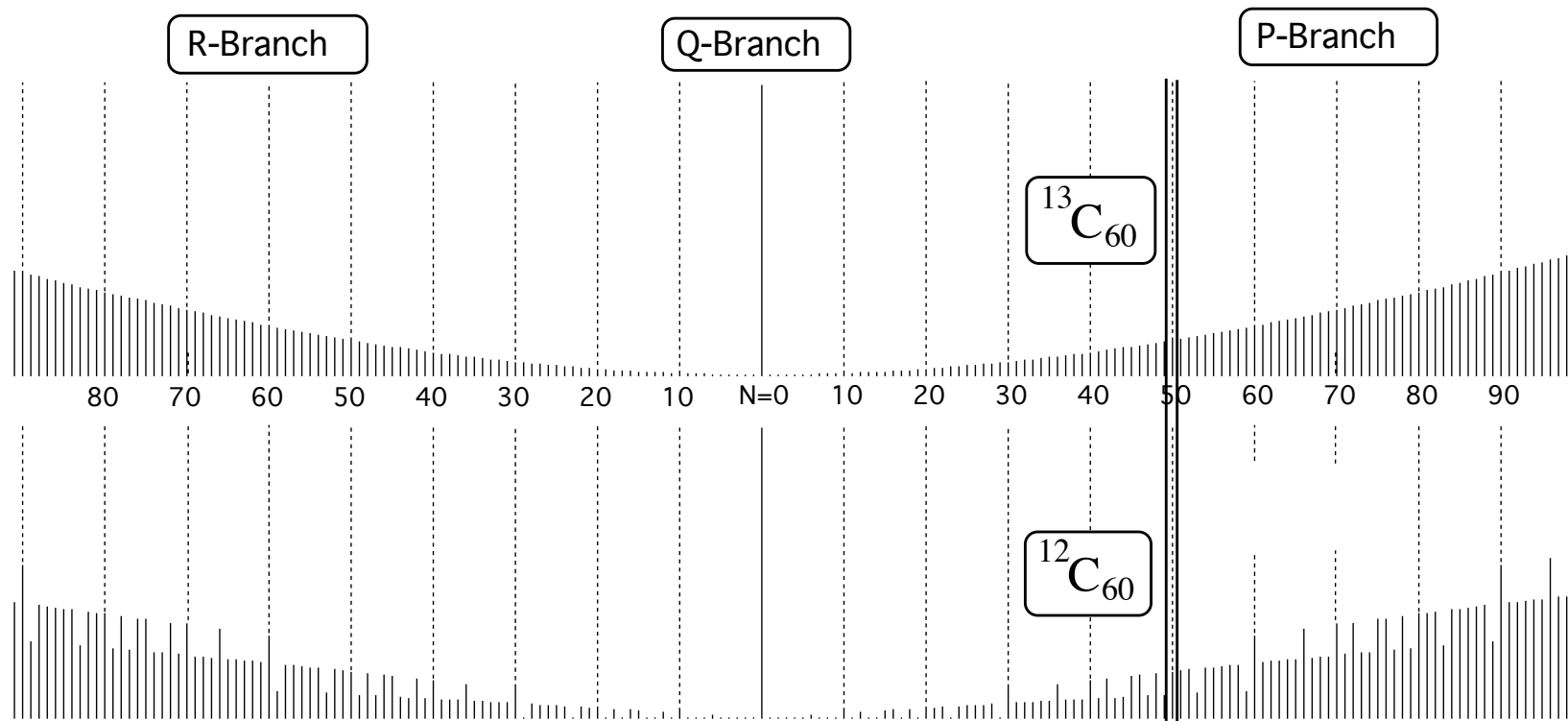
Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p=h=7.6 \times 10^5$ dyn/cm and $\pi=\eta=0.7 \times 10^5$ dyn/cm. The scale is in units of 1185 cm^{-1} . Lines a-d correlate with eigenmodes in fig. 4.

choices of spring constants. Comparison of the results obtained using icosahedral projection is made with those obtained by independently derived analytic formulas.

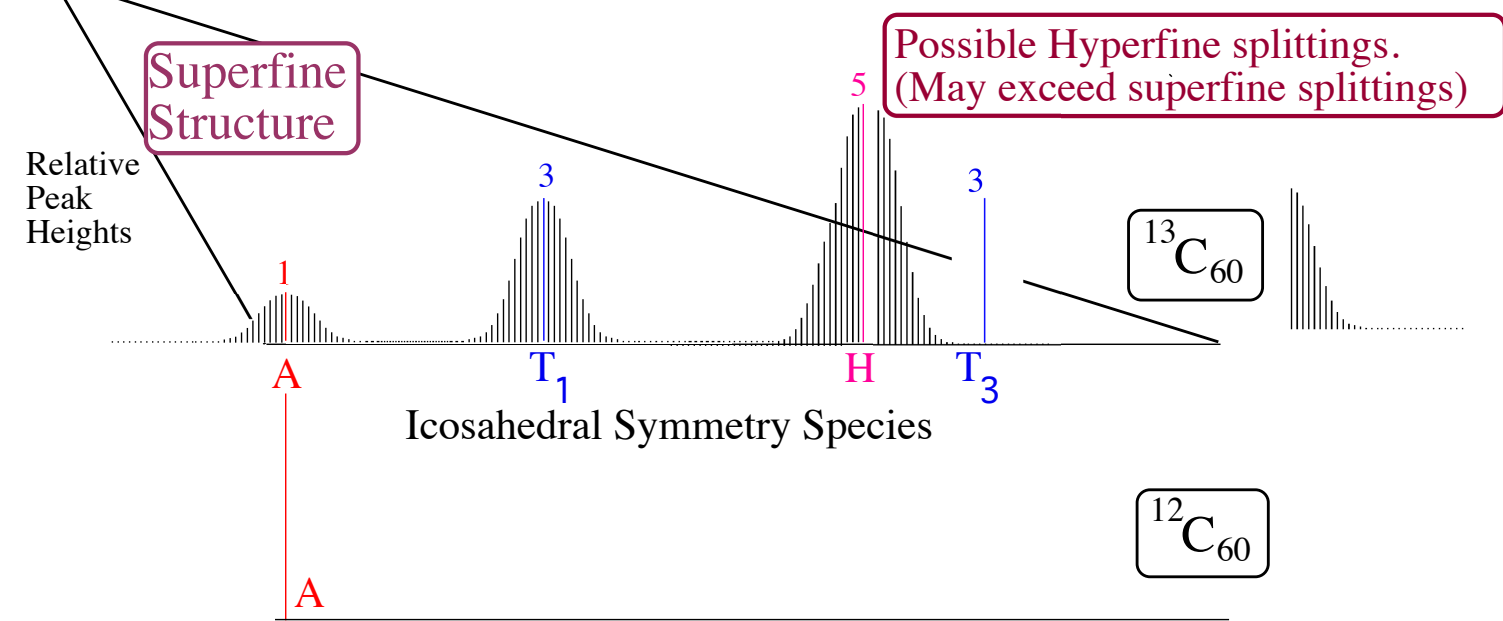
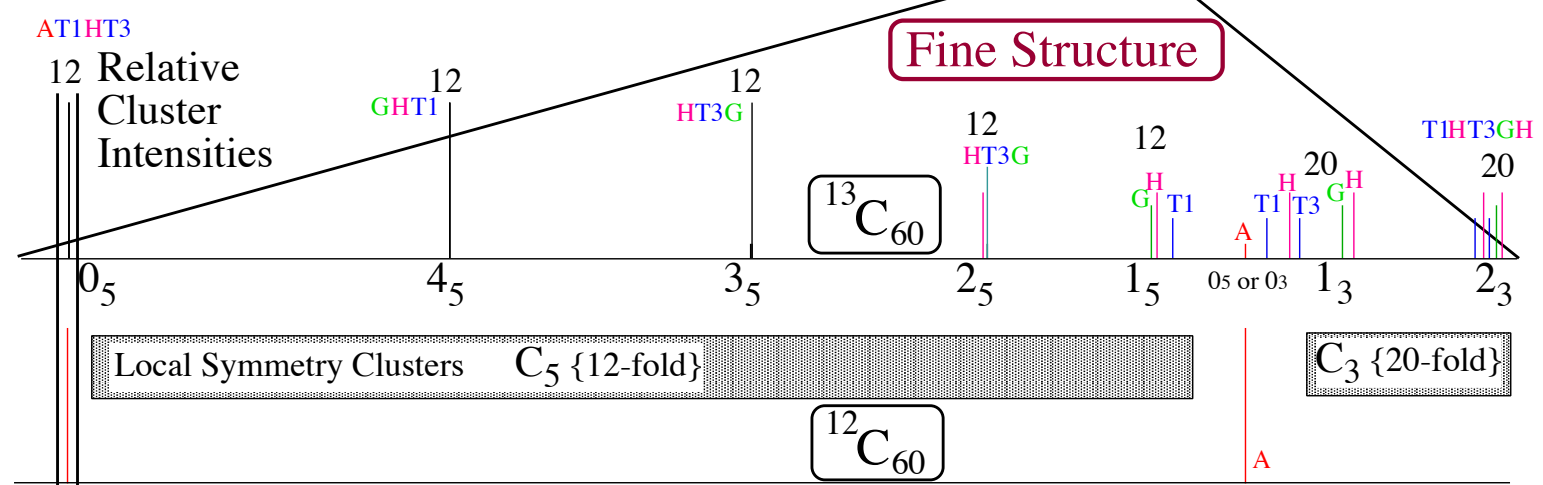
These four choices are:

(i) $p=\pi=\eta=0$, $h=1$. Here we have isolated 30 carbon atom pairs each aligned 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 programmed 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

Possible C_{60} Rovibrational Structure



$J=50$
 Fine structure
 comparing
 $^{13}C_{60}$ (2^{60} Hyperfine levels)
 with
 $^{12}C_{60}$ (1^{60} Hyperfine level)



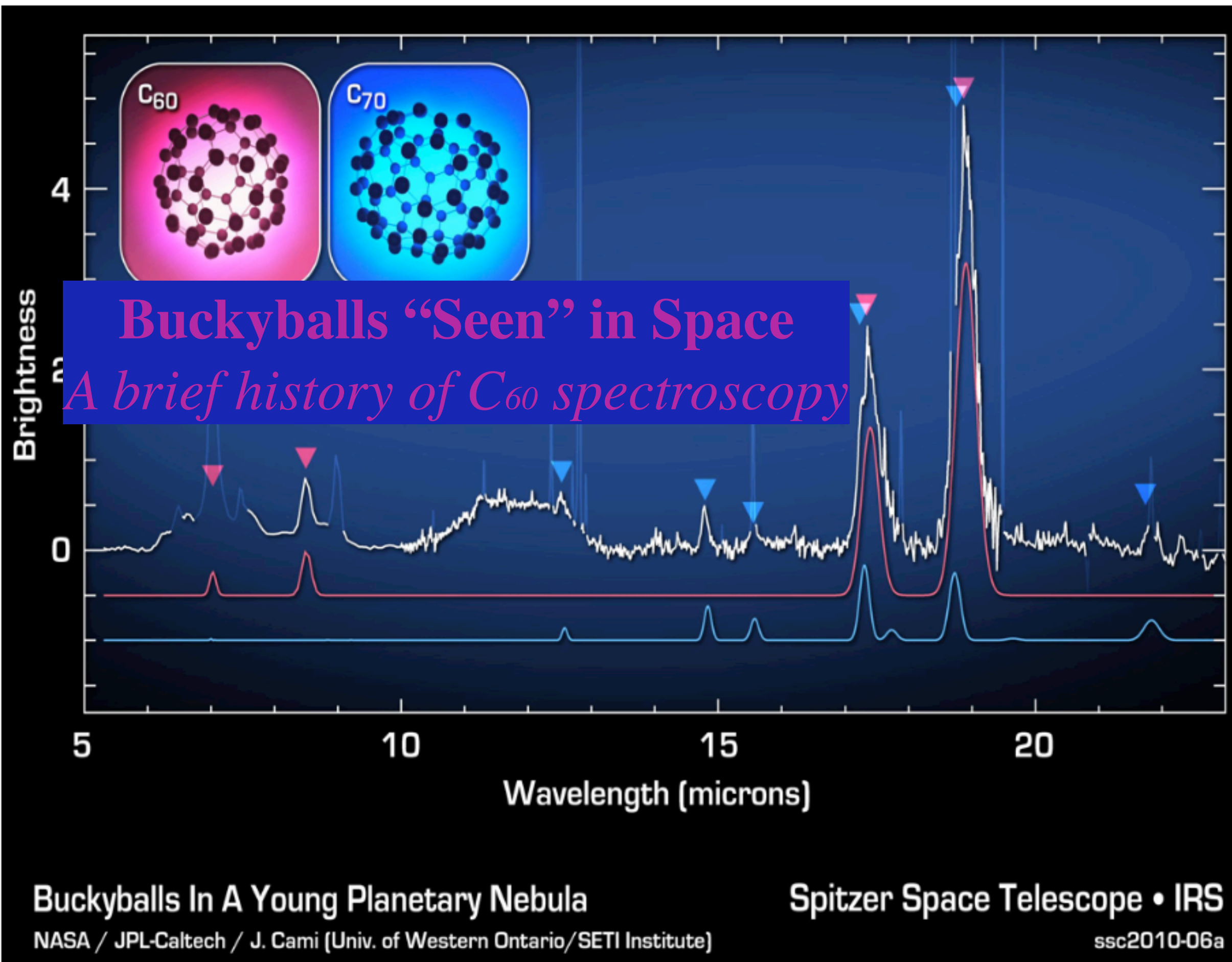
*W.G.Harter, D.E.Weeks,
 Chem. Phys. Letters 194,3(1992)*

Buckyballs “Seen” in Space

A brief history of C₆₀ spectroscopy

Bill Harter

UAF - Physics



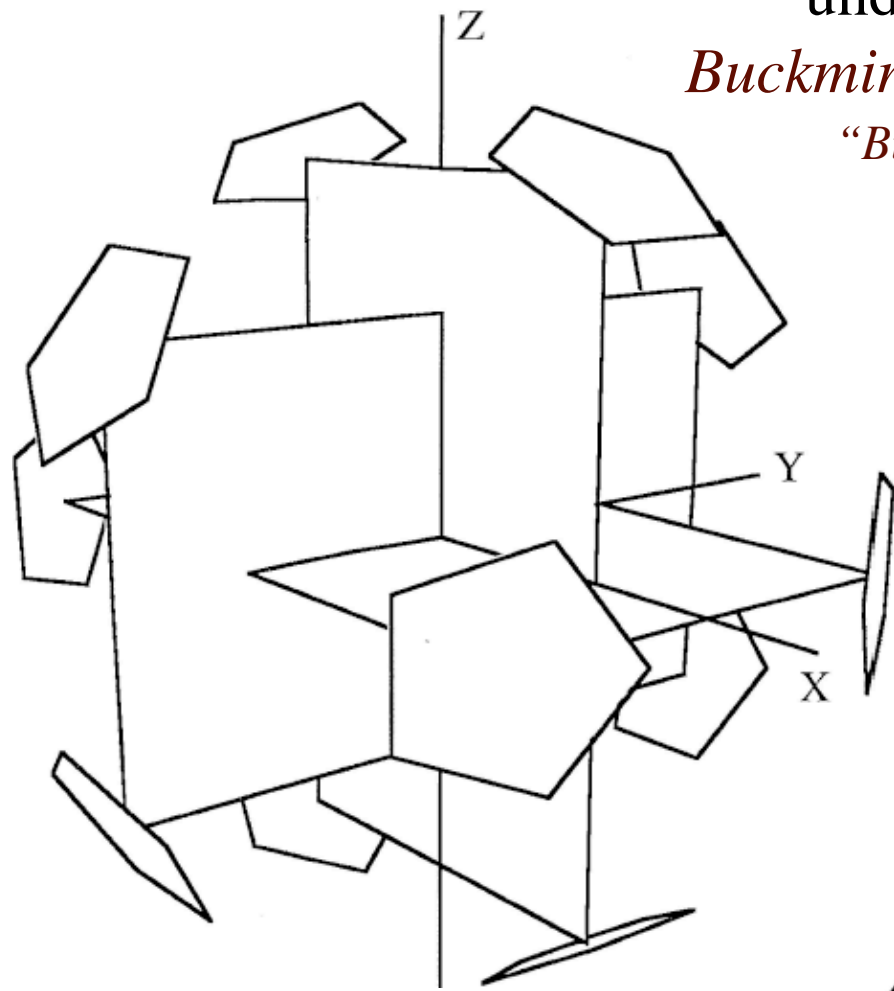
1st Try at “Seeing” in Lab
*Mass spectroscopy gives something
with atomic weight 720*

*Richard Smalley, Bob Curl, and Harry Kroto (1985)
Guess structure is C₆₀ “soccer ball”*

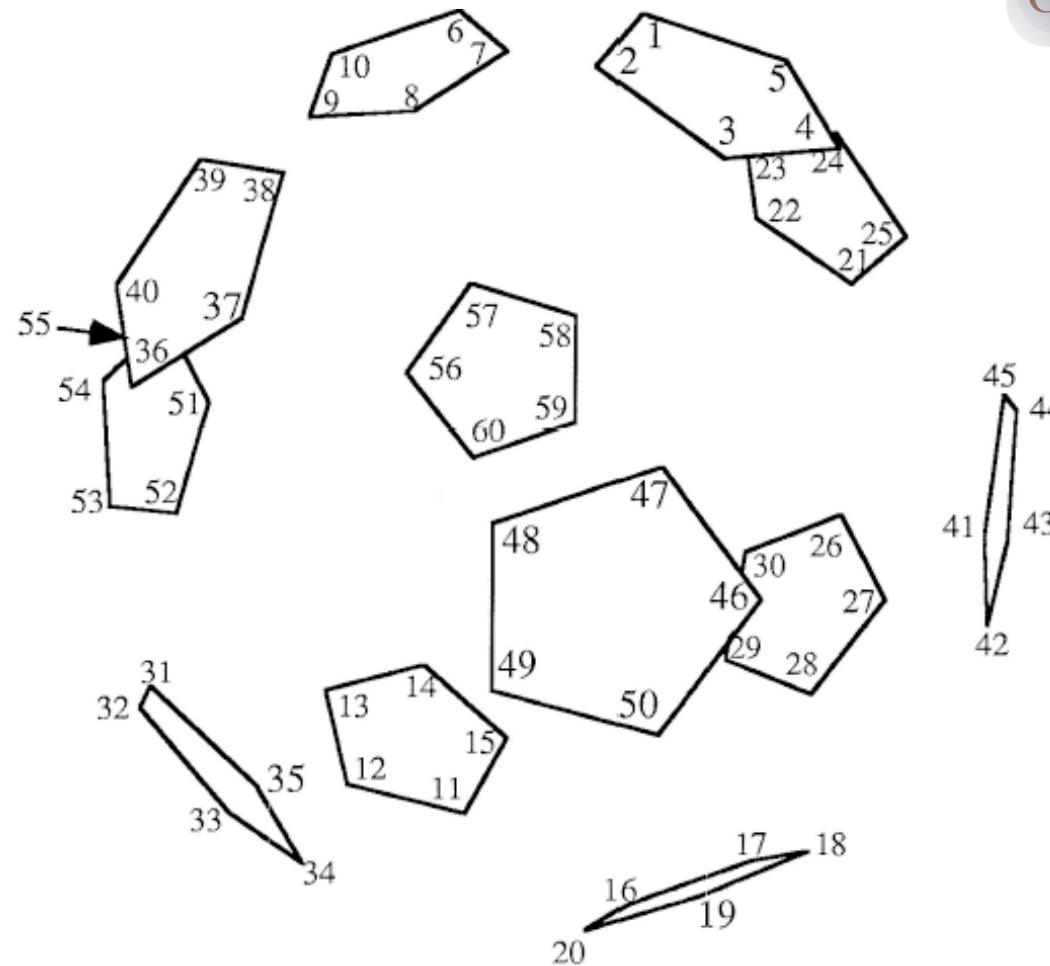
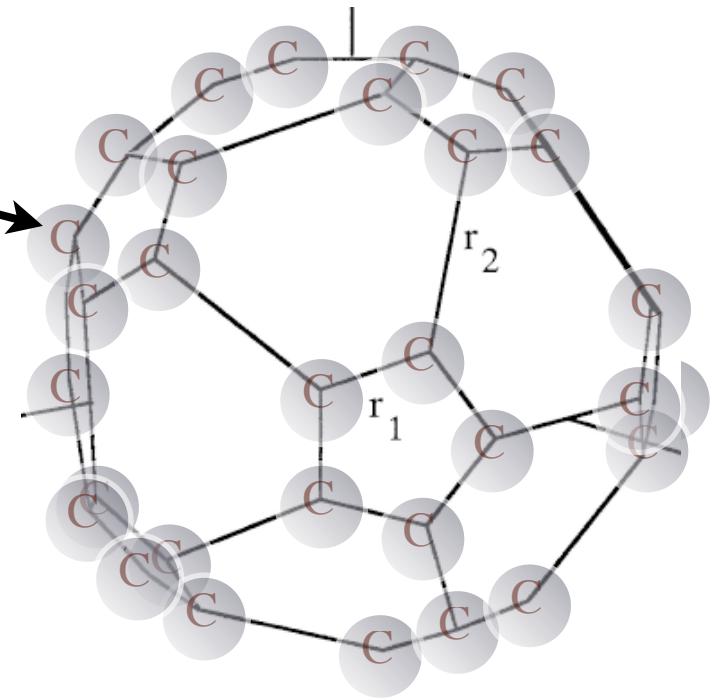
Three *Golden* rectangles
 (Ratio: $(\sqrt{5}+1)/2 : 1 = 1.618\dots$)

underlie C_{60}

Buckminsterfullerene
 "Buckyball"



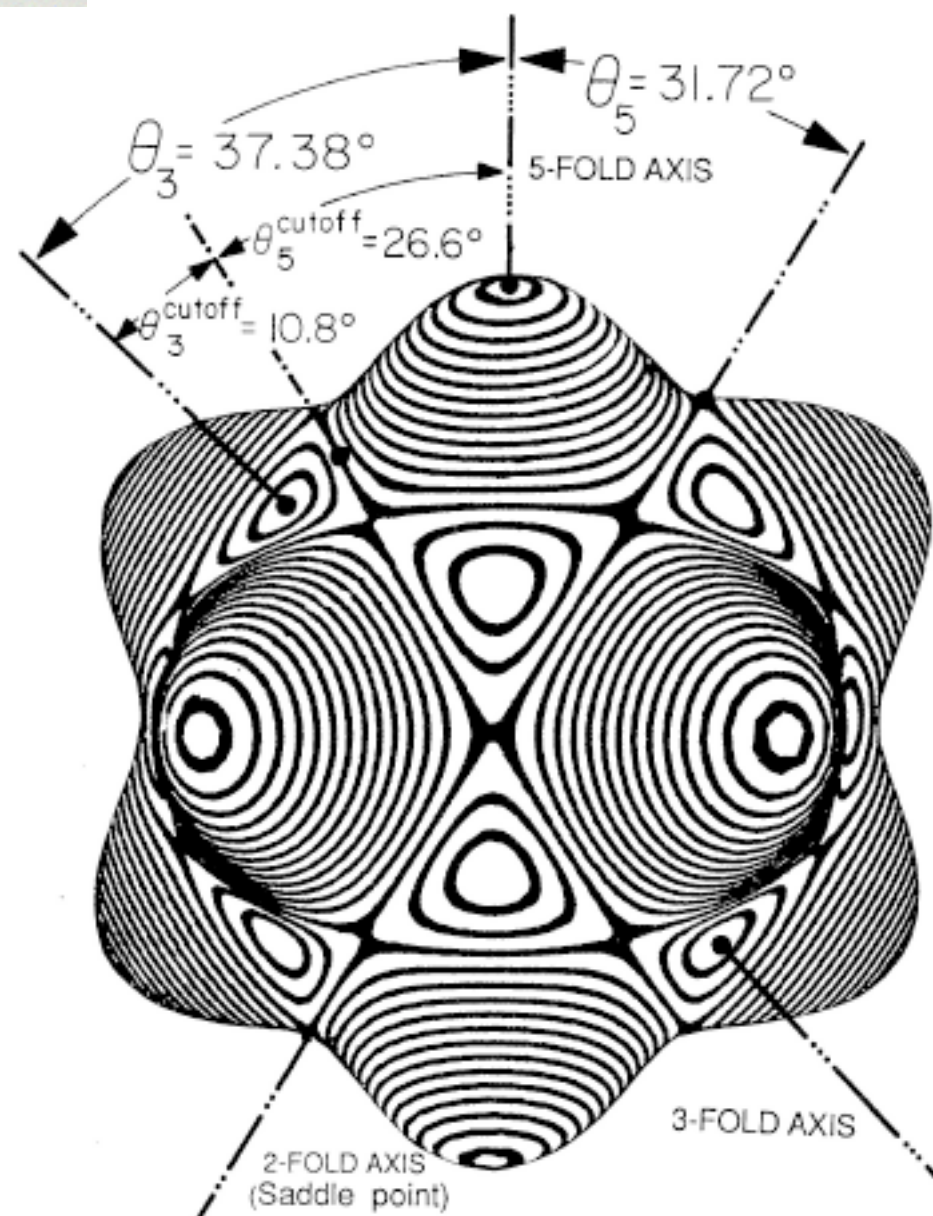
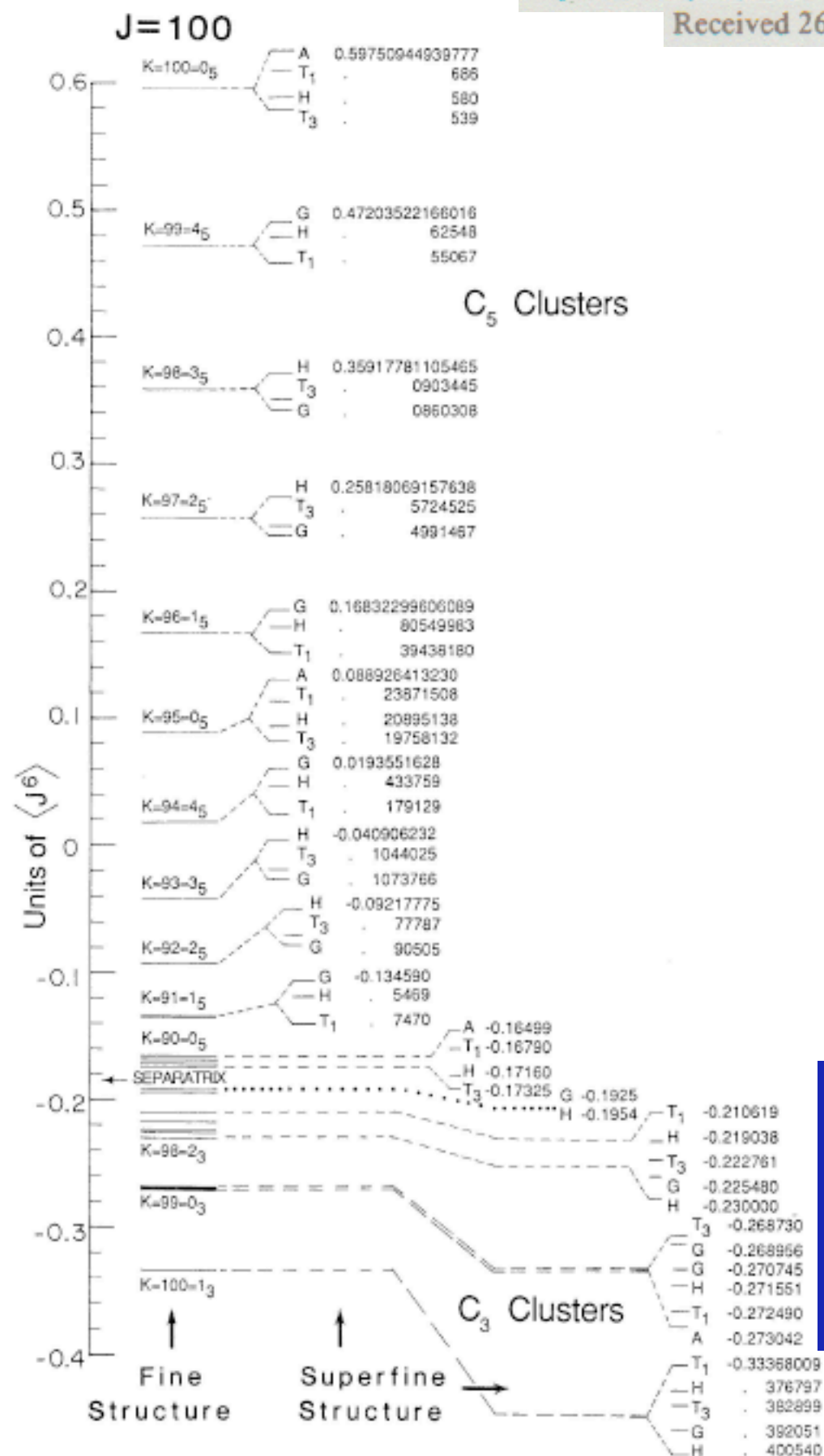
60 C atoms:
 one C at each
 vertex
 of a
Soccerball



William G. HARTER and David E. WEEKS

Department of Physics, J. William Fulbright College, University of Arkansas, Fayetteville, AR 72701, USA

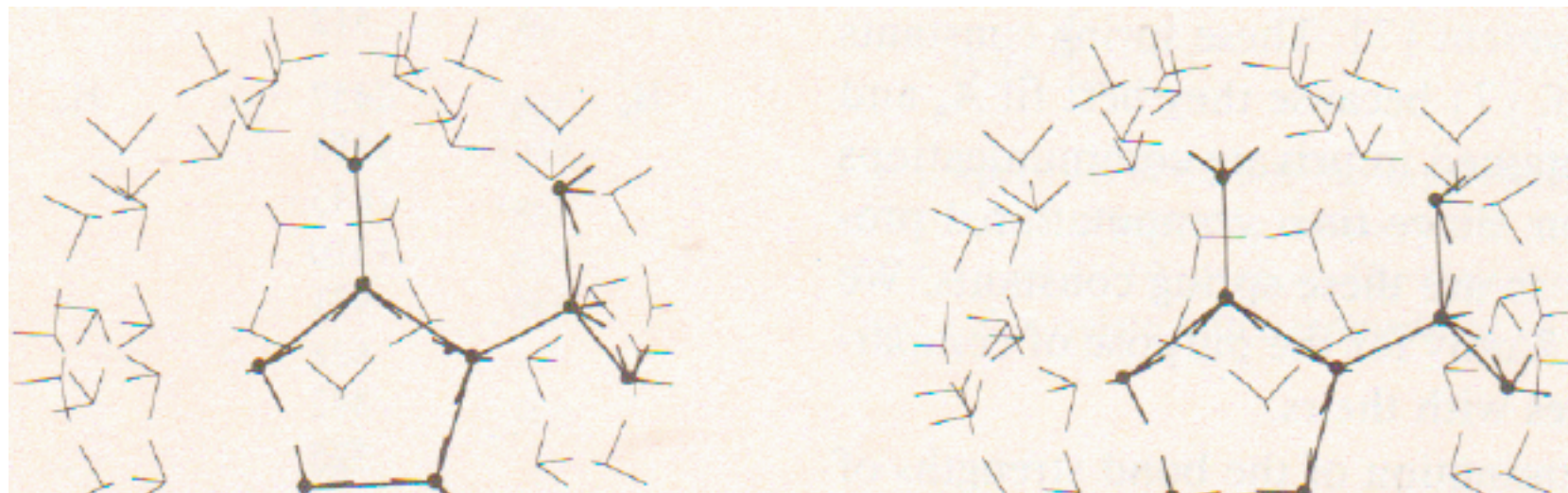
Received 26 August 1986



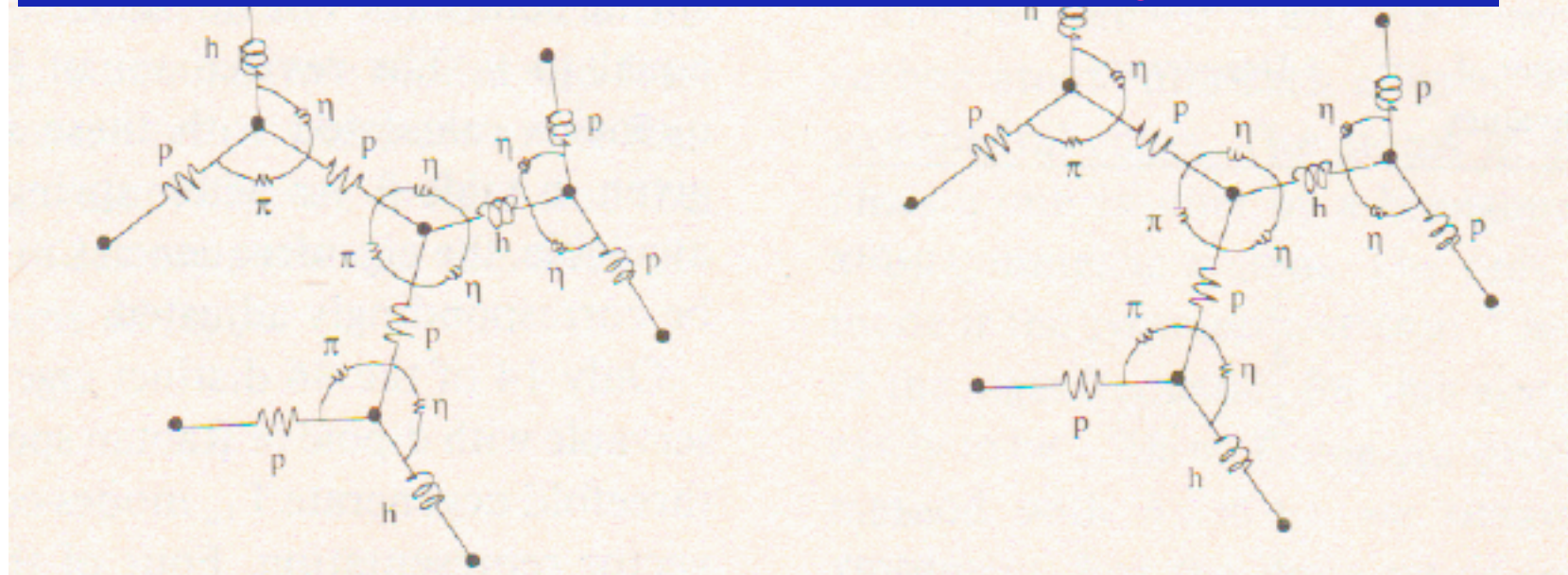
2nd Try at "Seeing" in Lab
Rotational spectroscopy predicted
(but still too hard to see)

$3 \cdot 60 = 180$ 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)

Volume 144, number 4

CHEMICAL PHYSICS LETTERS

4 March 1988

Table 3
Symmetry-labeled eigenfrequencies of Buckyball for $p=h=7.6 \times 10^5$ dyn/cm, $\pi=\eta=0.7 \times 10^5$ 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_{3g}	1900	T_{3u}	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		

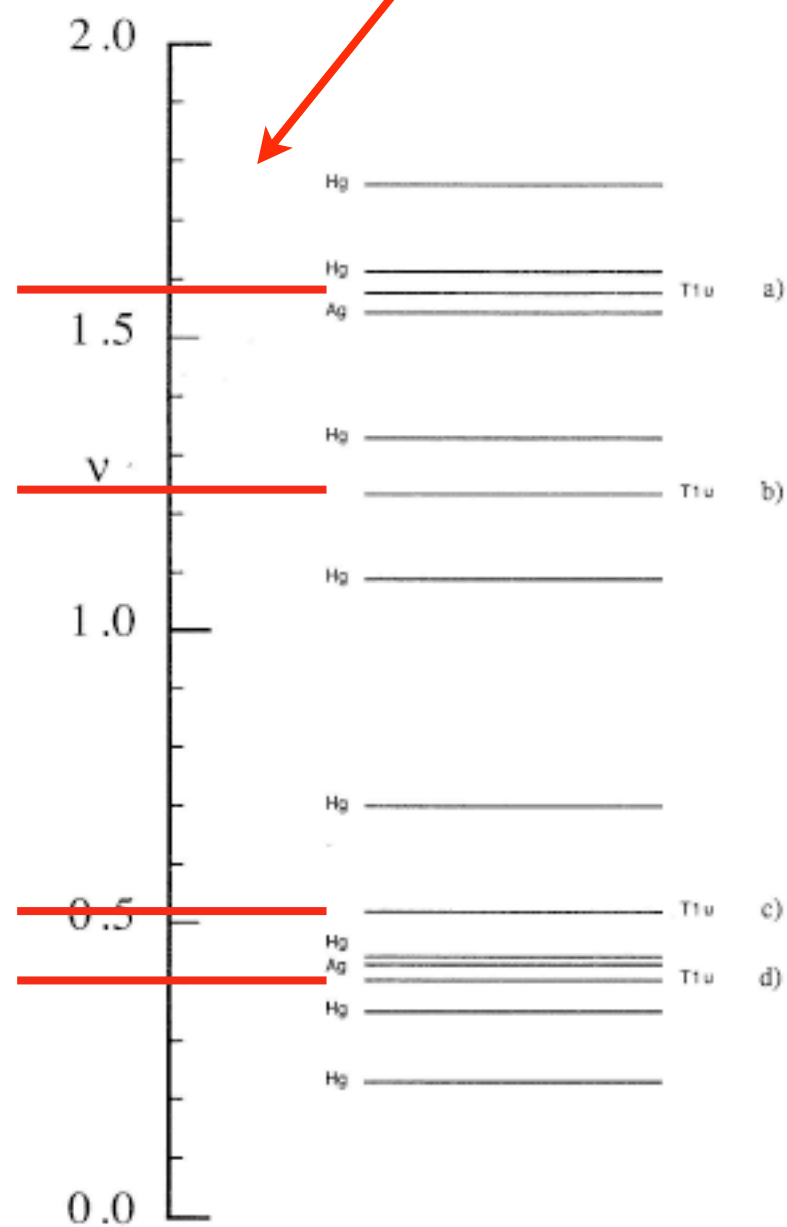
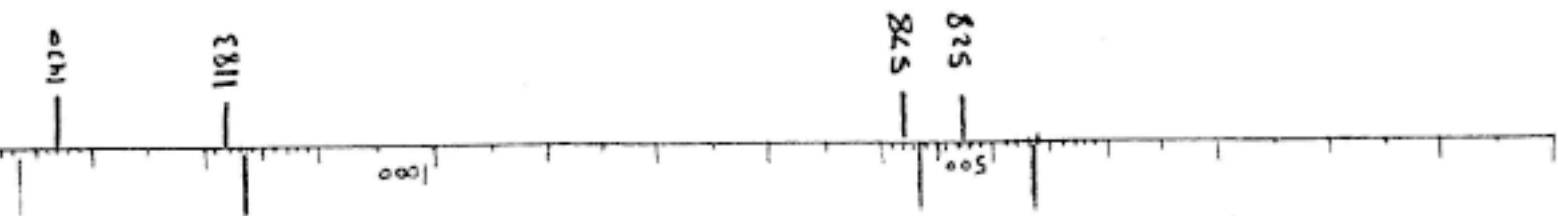


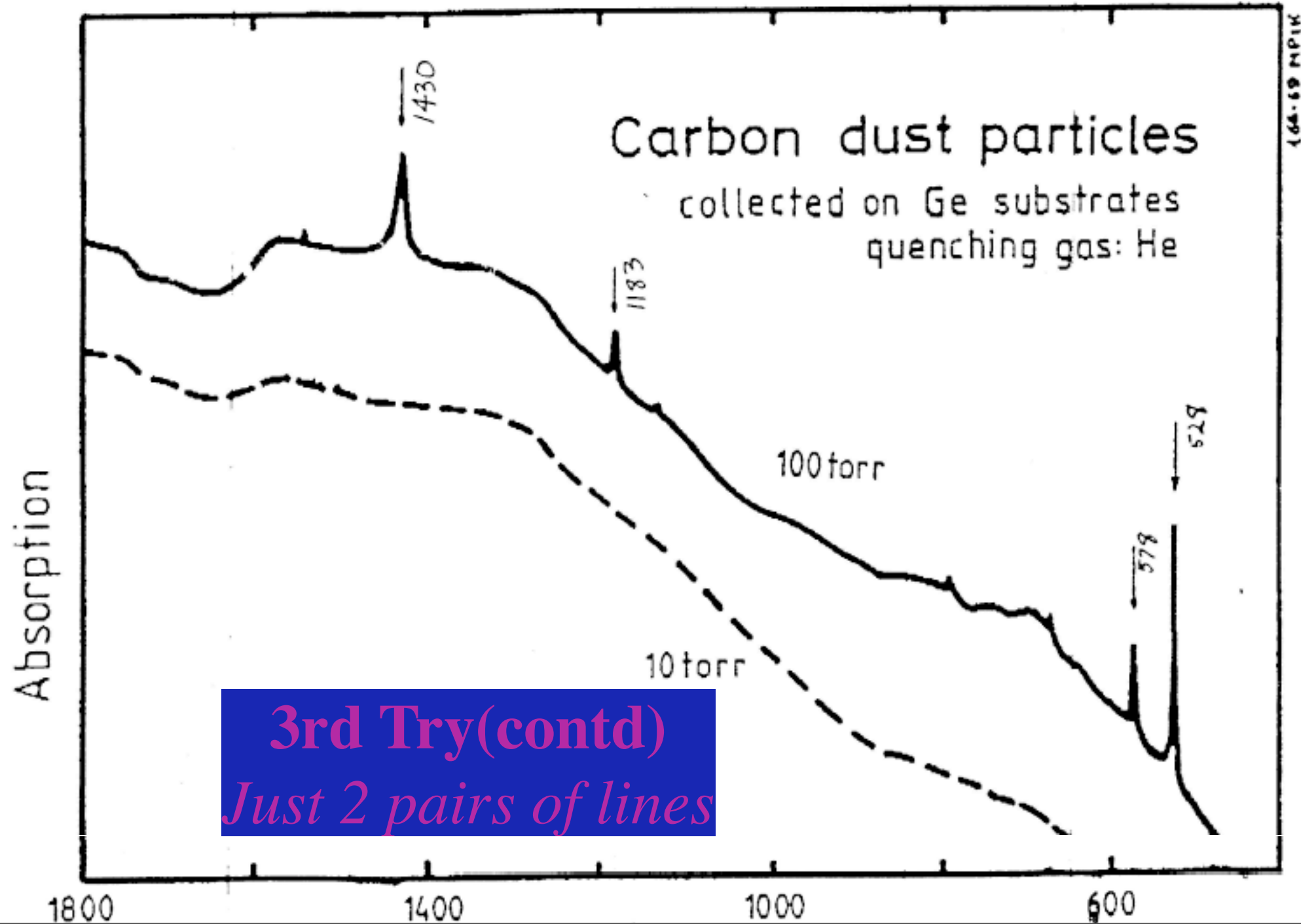
Fig. 3. Spectrum of the possibly dipole and Raman active modes of Buckyball. The spring constants are $p=h=7.6 \times 10^5$ dyn/cm and $\pi=\eta=0.7 \times 10^5$ dyn/cm. The scale is in units of 1185 cm^{-1} . Lines a-d correlate with eigenmodes in fig. 4.

Experiment:
p=h - Spring Model:

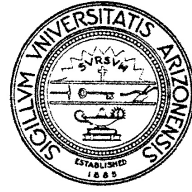


Date: W. Kratschmer, K. Fostiropoulos
Don R. Huffman

Max Planck
U of Arizona



3rd Try(contd)
Just 2 pairs of lines



THE UNIVERSITY OF ARIZONA
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 C₆₀ 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.

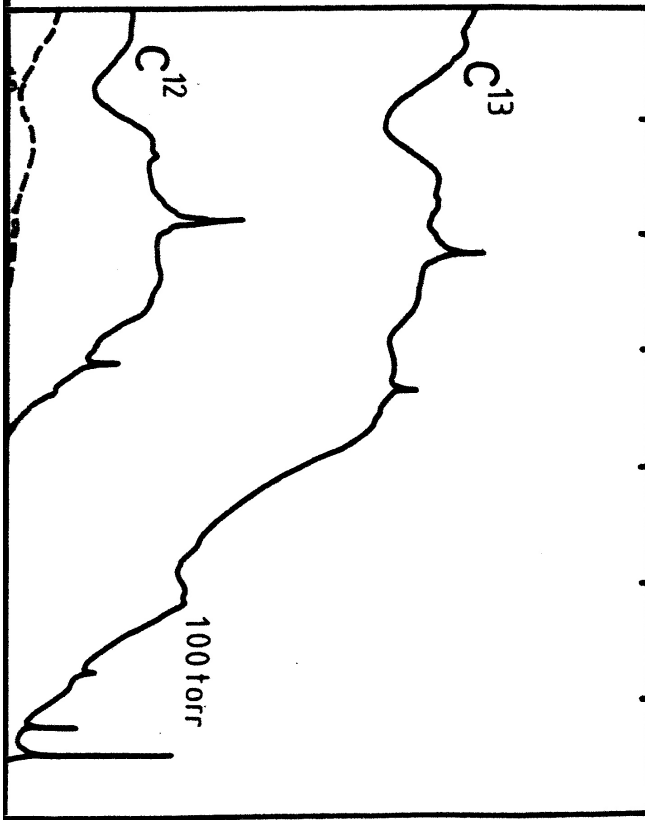
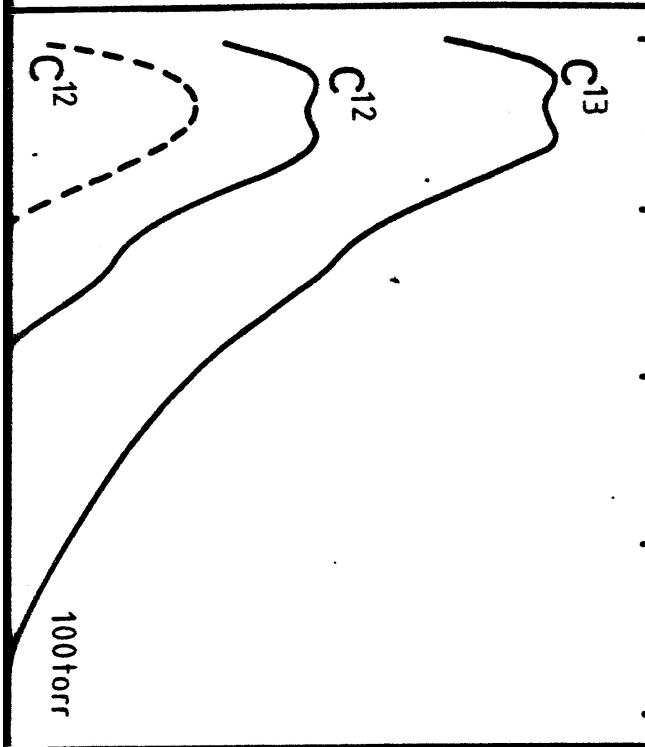
Sincerely,

Donald R. Huffman
Professor of physics

DRH
Incl.

Fig D.R. 2

ORPTION (-logT)



21-90 NP18

Carbon dust particles
quenching gas: He

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.”

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.



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)

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

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



