Based on QTCA Lectures 24-25
(2013)
and
AMOP Lectures 17-18 (2014)

Group Theory in Quantum Mechanics
Lecture 27 (4.30.15)
Introduction to Rotational Eigenstates and Spectra II

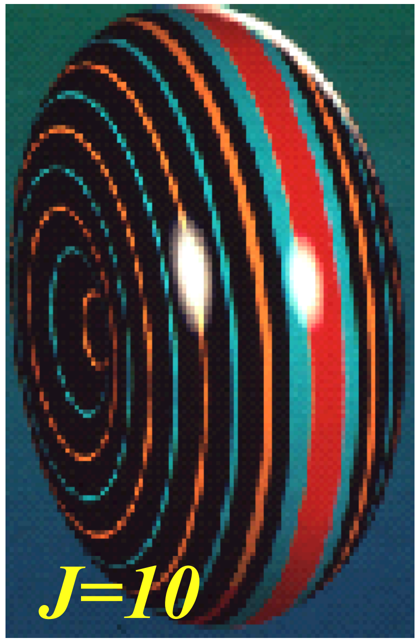
Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25 ,Computer Phys. Reports 8,319-394 (1988)
(PSDS - Ch. 5, 7)

Review: Asymmetric rotor levels of $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ and RES plots
  $D_2 \supset C_2$ symmetry correlation
Review: Spherical rotor levels and RES plots
  Spectral fine structure of SF_6, SiF_4, C_8H_8,...
  $O \supset C_4$ and $O \supset C_3$ symmetry correlation
    Some more examples of J=30 levels (including $\mathbf{T}^{[6]}$ vs $\mathbf{T}^{[4]}$ effects)
Details of $P(88)$ ν_4 SF_6 and $P(54)$ ν_4 CF_4 spectral structure and implications
  Beginning theory
  Rovibronic nomograms and PQR structure
  Rovibronic energy surfaces (RES) and cone geometry
  Spin symmetry correlation, tunneling, and entanglement
    Hyperfine vs. superfine structure (Case 1. vs Case 2.)
    Spin-0 nuclei give Bose Exclusion
      The spin-symmetry species mixing problem
  Analogy between PE surface dynamics and RES
  Rotational Energy Eigenvalue Surfaces (REES)

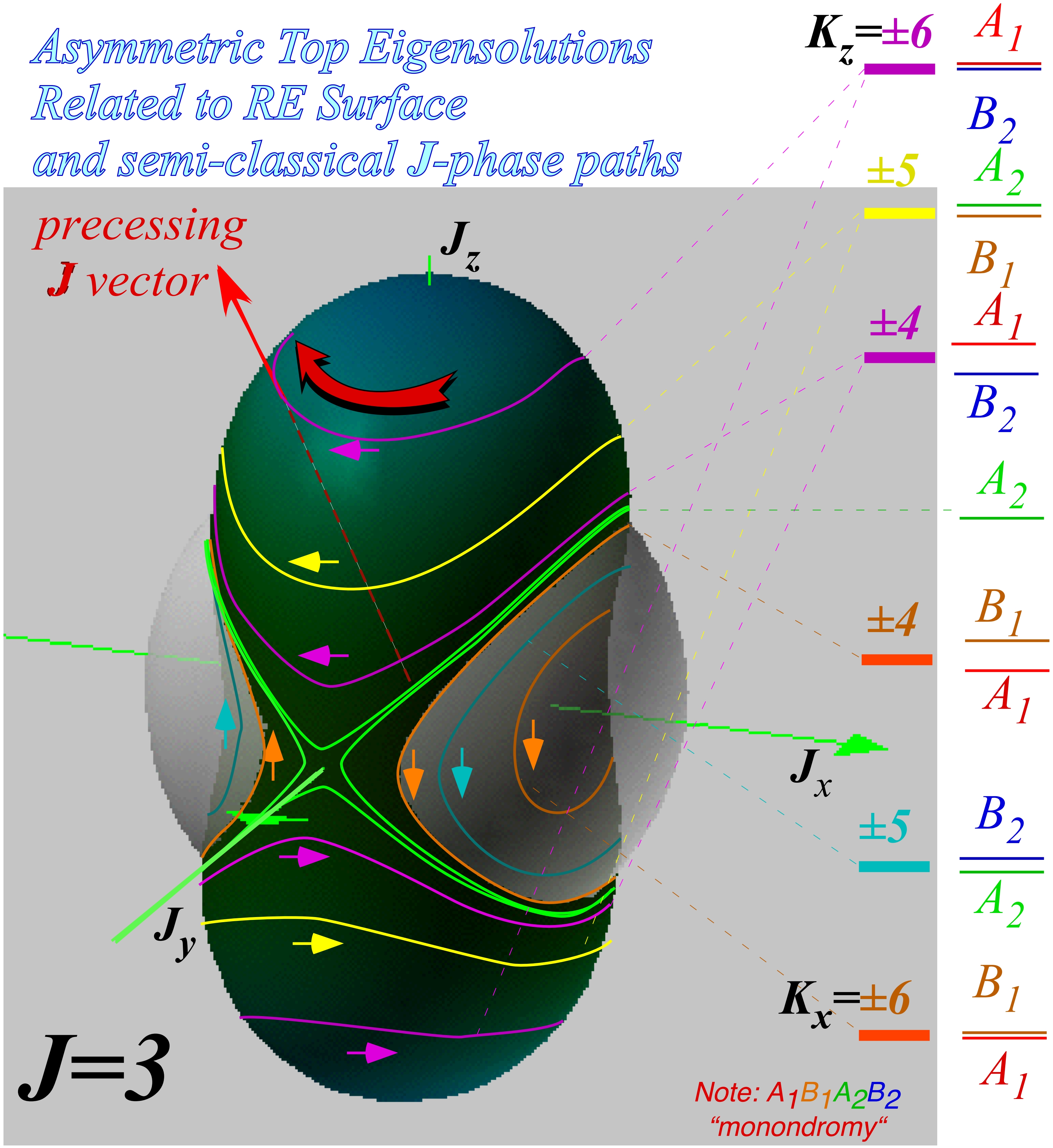
➡ *Review: Asymmetric rotor levels of* $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *and RES plots*

$D_2\supset C_2$ symmetry correlation

Review: Symmetric vs. Asymmetric rotor levels



Asymmetric Top Eigensolutions
Related to RE Surface
and semi-classical J-phase paths

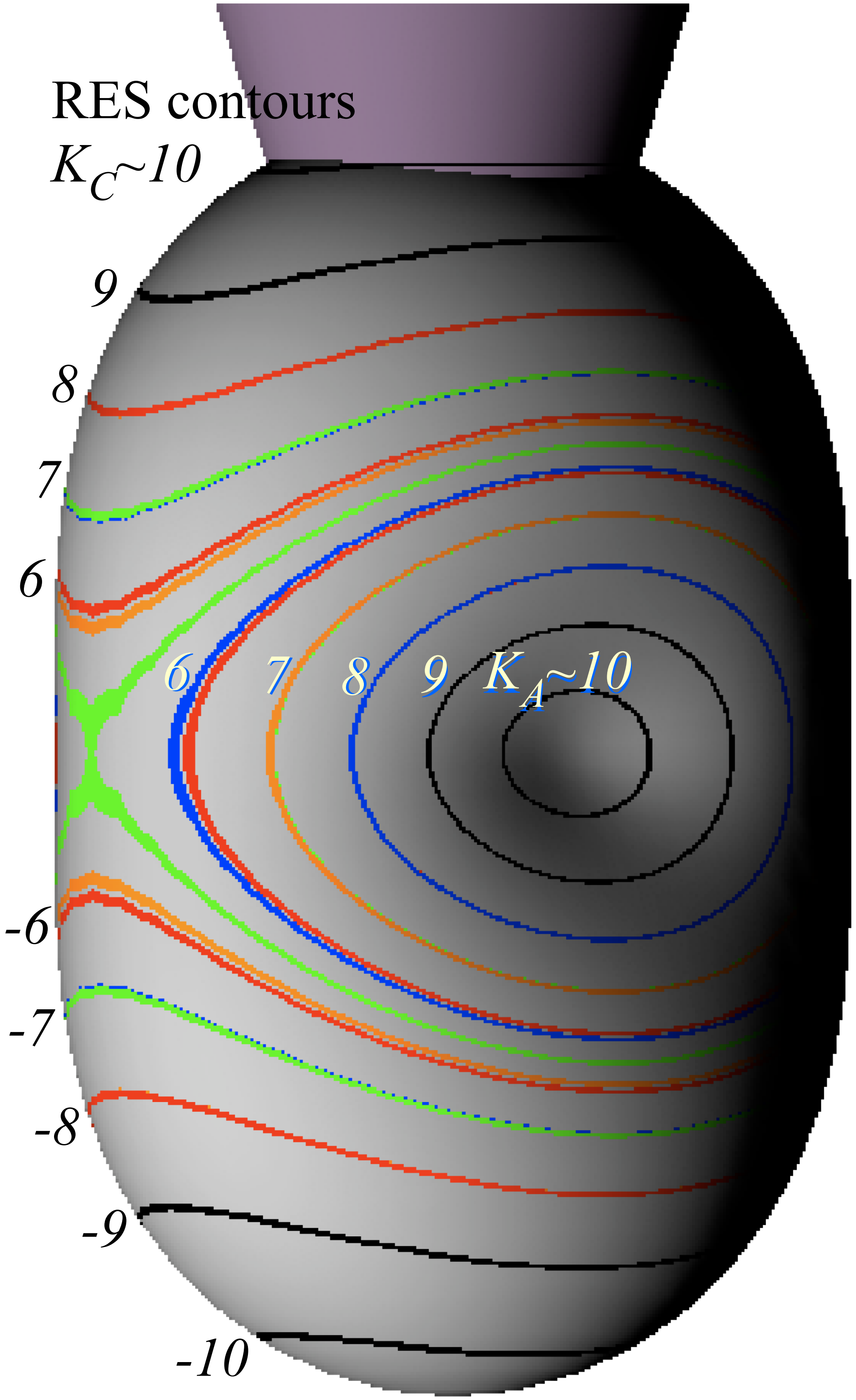


Note: $A_1B_1A_2B_2$
“monondromy“

after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

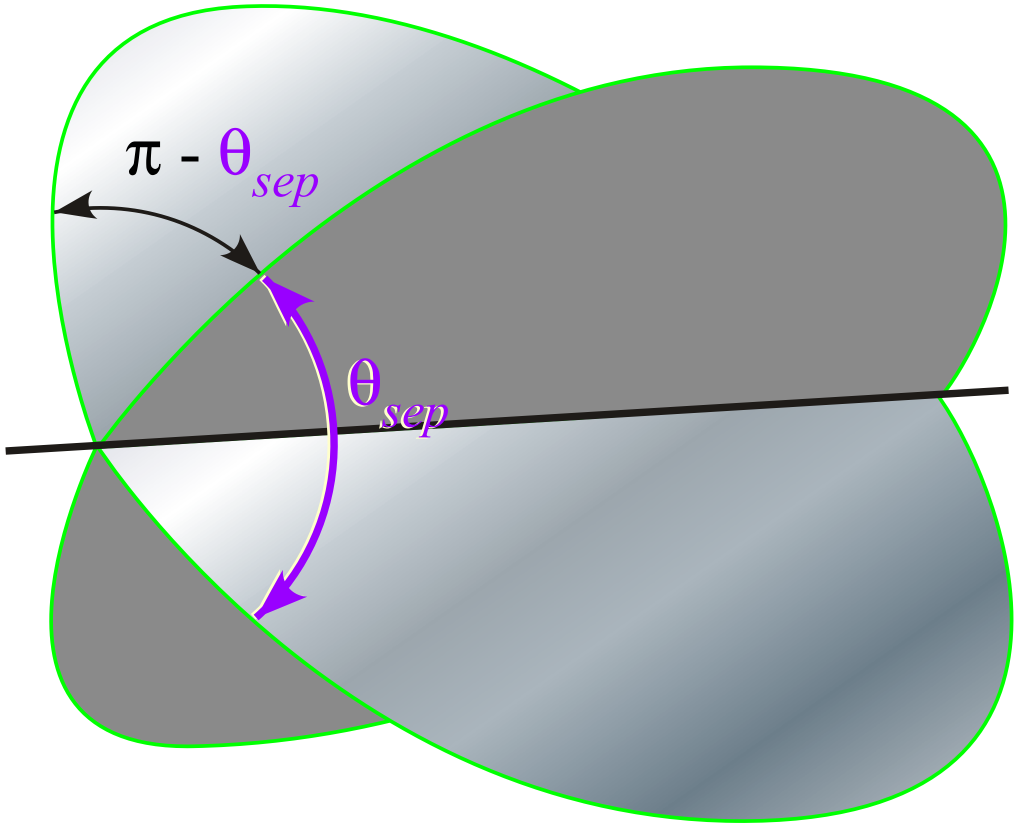
Review: Asymmetric rotor levels

RES contours K_C~*10*



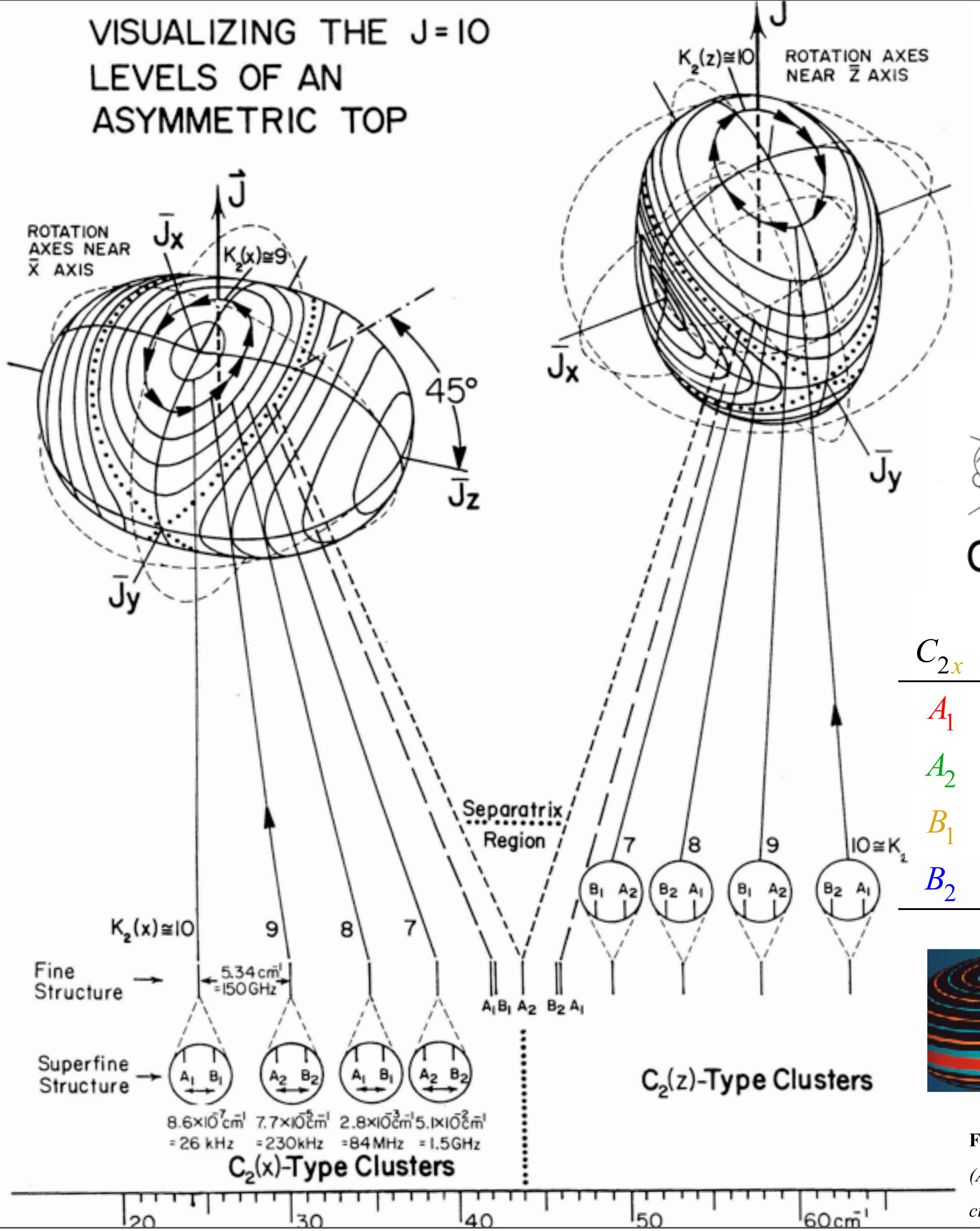
Separatrix circle pair
dihedral angle

$$\theta_{sep} = \text{atan}\left(\frac{A-B}{B-C}\right)$$



Int.J.Molecular Science 14.(2013) Fig.3 p. 733

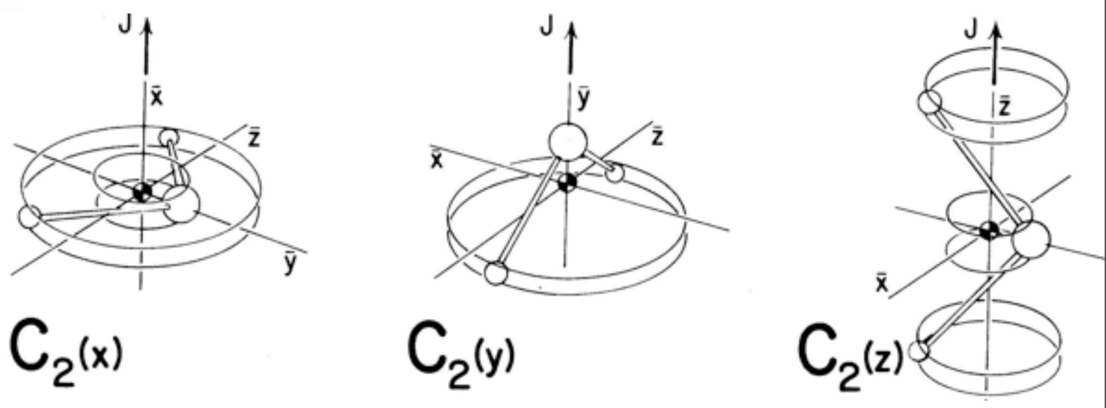
VISUALIZING THE J=10 LEVELS OF AN ASYMMETRIC TOP



D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

Examples of Group⊃Sub-group correlation

$D_2\supset C_2(x)$ *$D_2\supset C_2(y)$* *$D_2\supset C_2(z)$*



C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

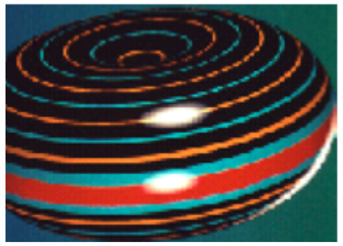


Fig. 25.4.2 *$J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*

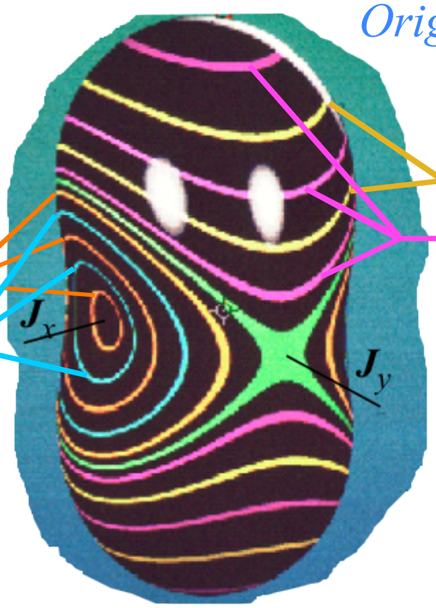
Review: Asymmetric rotor levels of $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *and RES plots*

➡ *$D_2 \supset C_2$ symmetry correlation*

Examples of Group⊃Sub-group correlation

$D_2 \supset C_2(x)$ $D_2 \supset C_2(y)$ $D_2 \supset C_2(z)$

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1



Original color mixing scheme gives

yellow $1_2=(A_2B_1)$

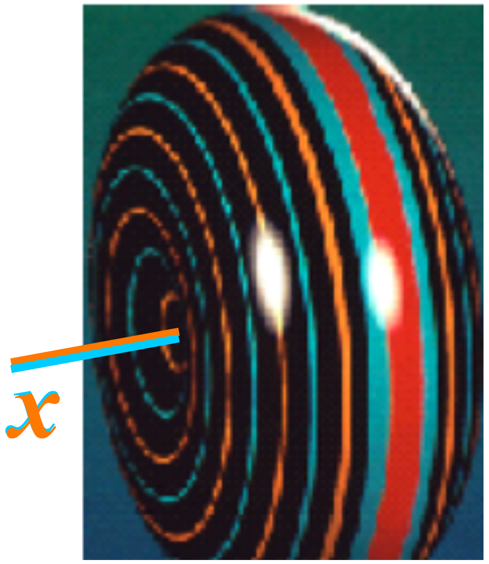
purple $0_2=(A_1B_2)$

for z-prolate axis

orange $0_2=(A_1B_1)$

cyan $1_2=(A_2B_2)$

for x-oblate axis

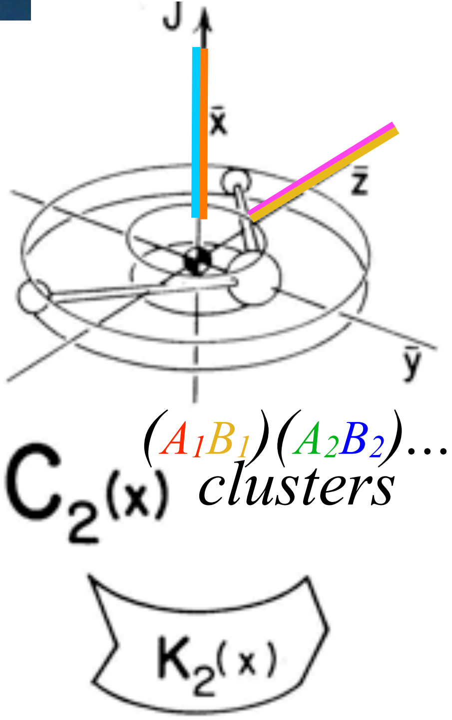


C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

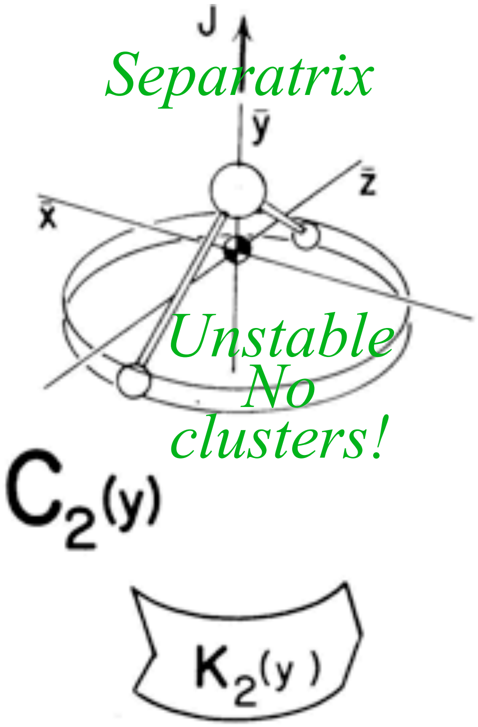
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

Review: Asymmetric vs Symmetric rotor levels

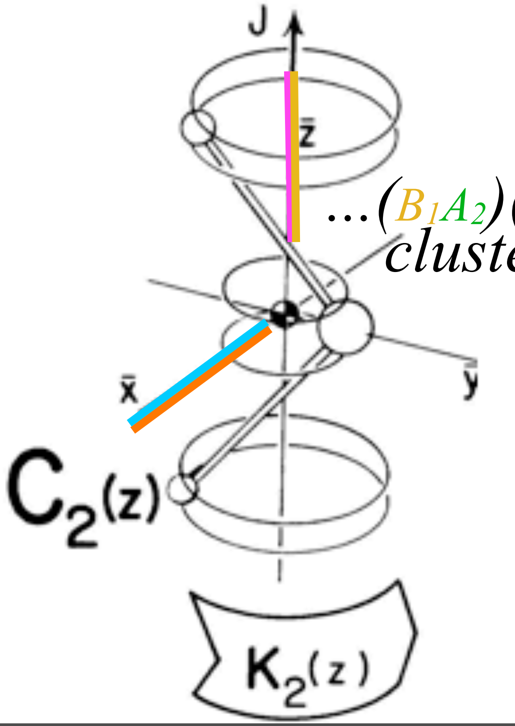


$(A_1B_1)(A_2B_2)$... clusters



Separatrix

Unstable No clusters!



...$(B_1A_2)(B_2A_1)$ clusters

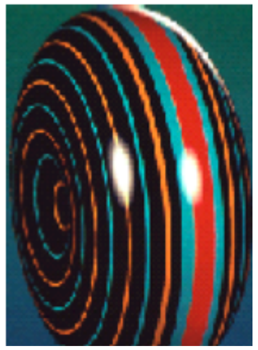
Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*

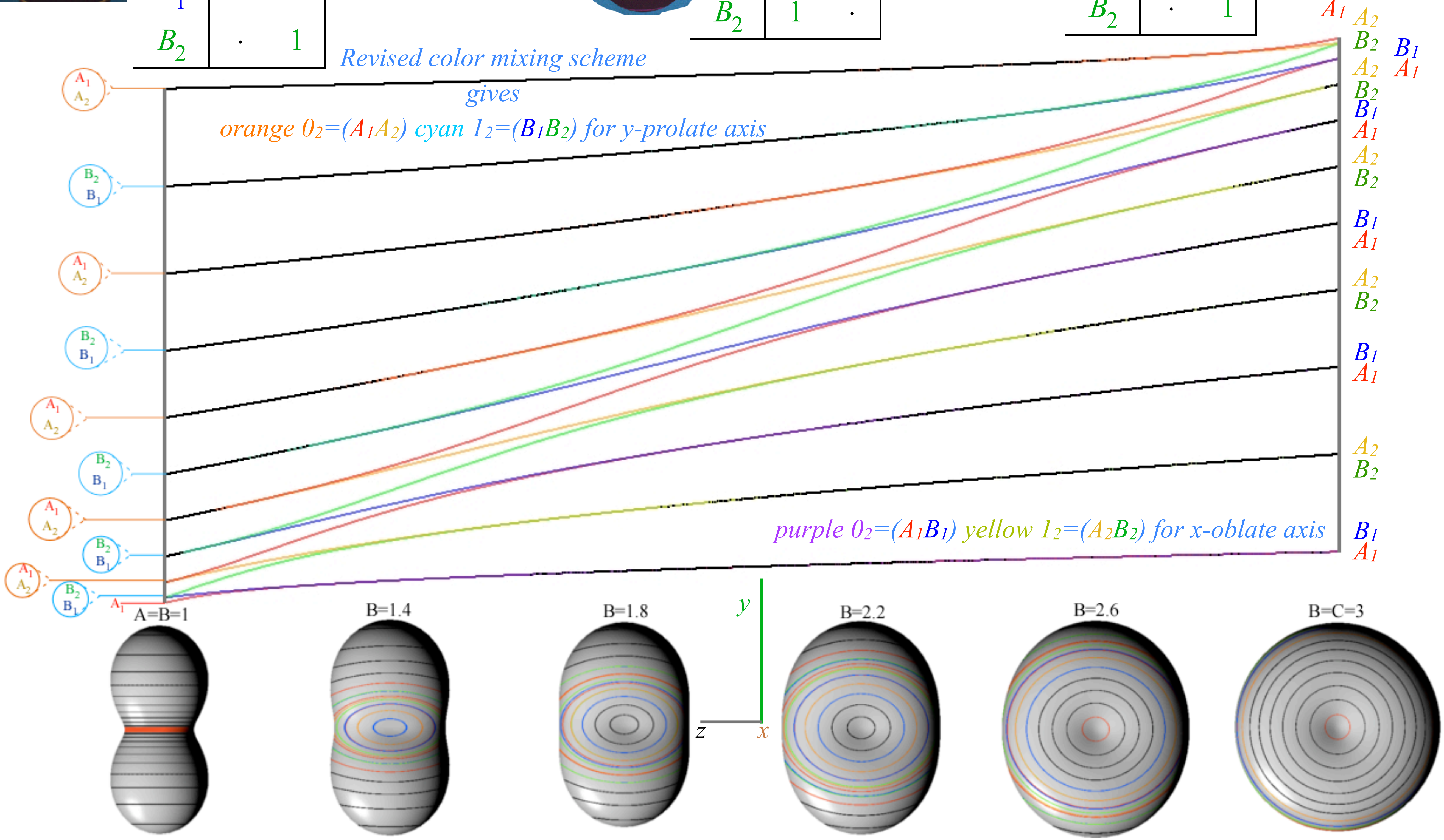
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1





Revised color mixing scheme

gives

orange $0_2=(A_1A_2)$ cyan $1_2=(B_1B_2)$ for y-prolate axis

purple $0_2=(A_1B_1)$ yellow $1_2=(A_2B_2)$ for x-oblate axis

(Revised color mixing scheme used here)

Int.J.Molecular Science 14.(2013) Fig.4 p. 734

Review: Spherical rotor levels and RES plots

➡ *Spectral fine structure of SF_6, SiF_4, C_8H_8,...*

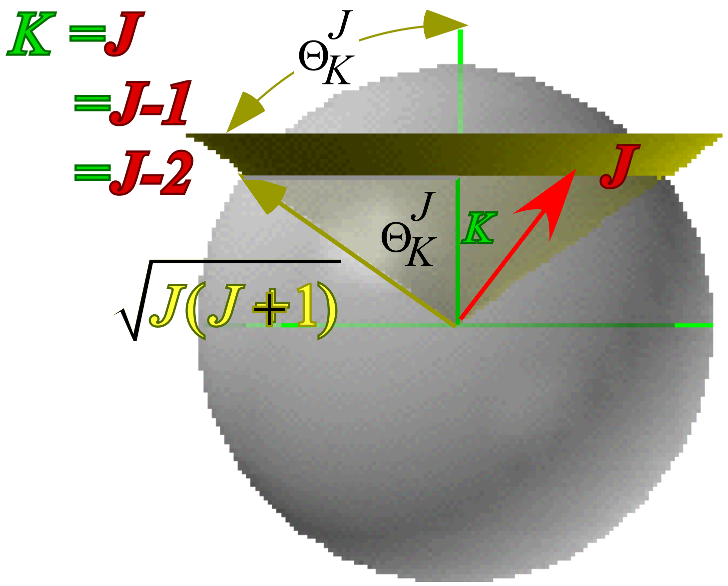
$O\supset C_4$ and $O\supset C_3$ symmetry correlation

Some more examples of J=30 levels (including $\mathbf{T}^{[6]}$ *vs* $\mathbf{T}^{[4]}$ *effects)*

Review: Spherical rotor levels

Finding Hamiltonian Eigensolutions by Geometry
using
Uncertainty Cone Angles

$$\cos\Theta_K^J = \frac{K}{\sqrt{J(J+1)}}$$

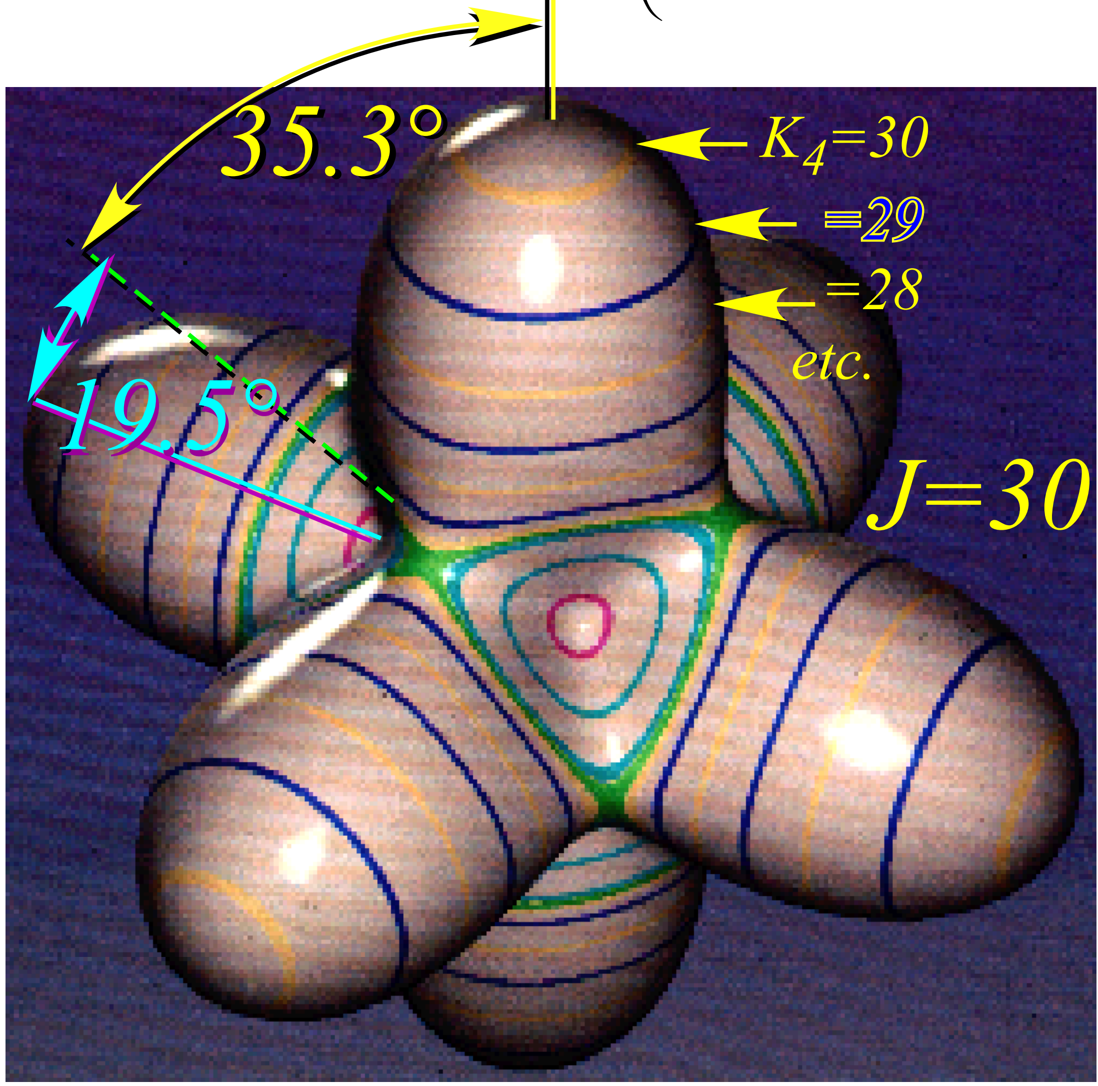


J *cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels*

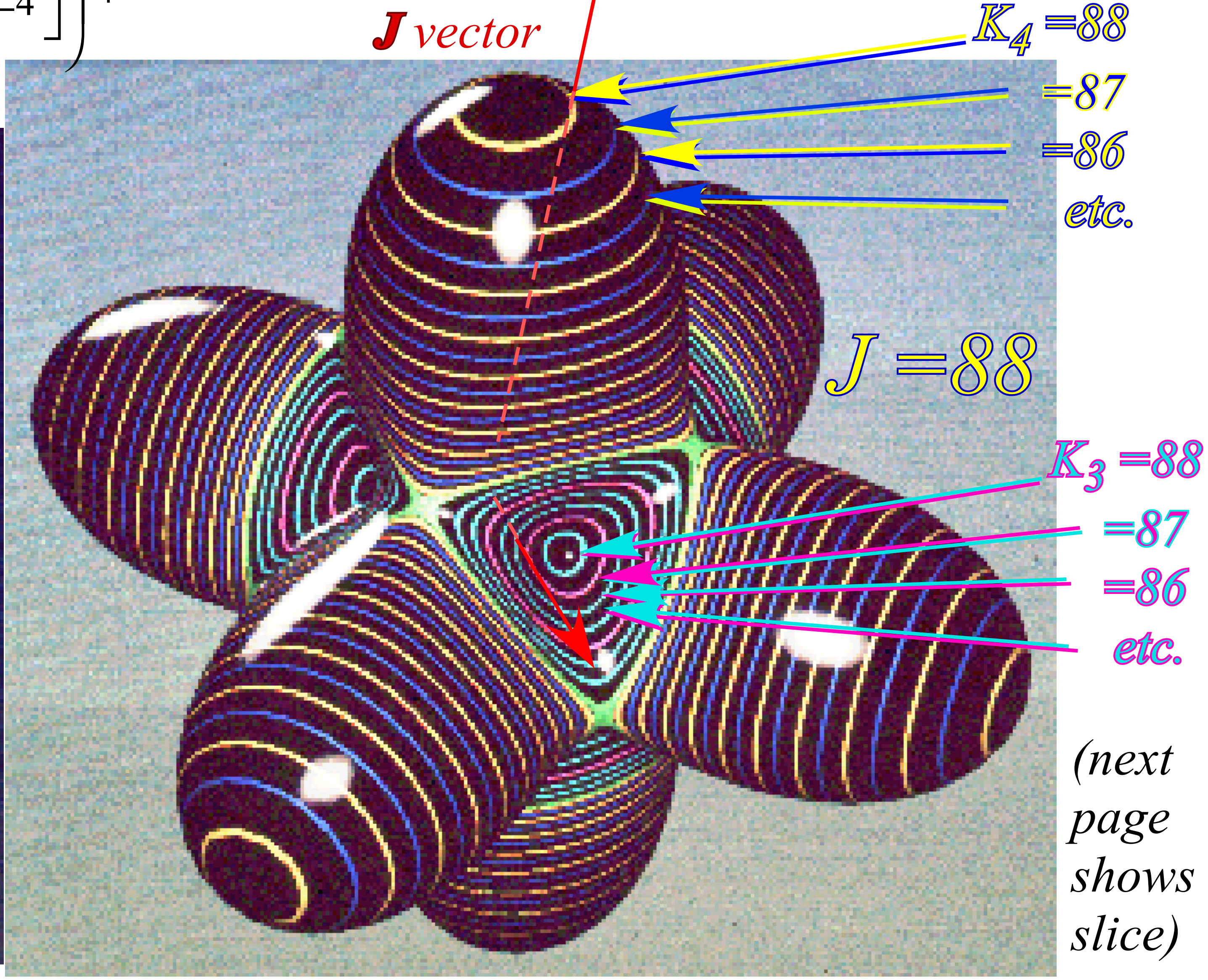
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

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

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

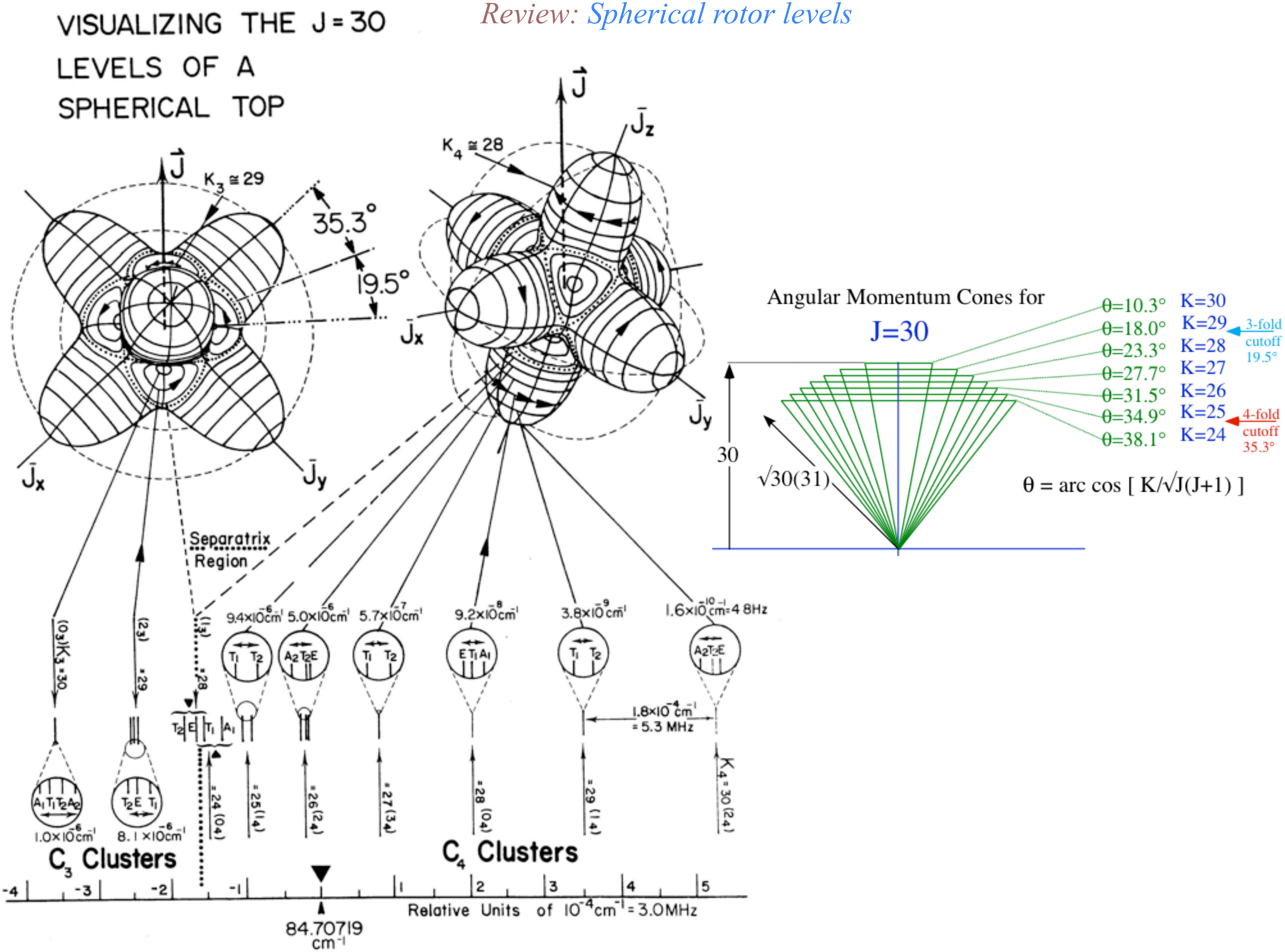


RE Surface topo-lines track precessing semi-classical ***J*** *vector*

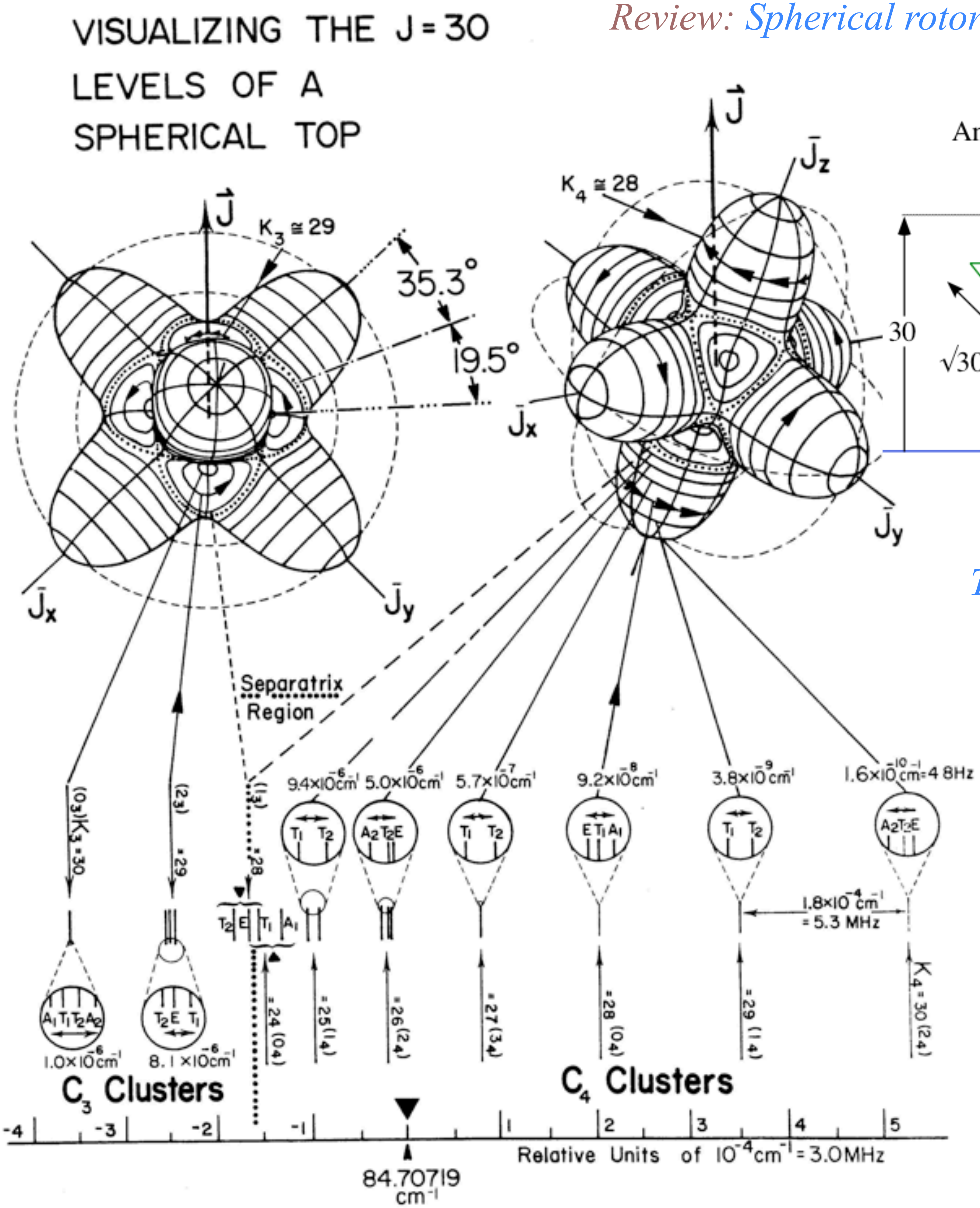


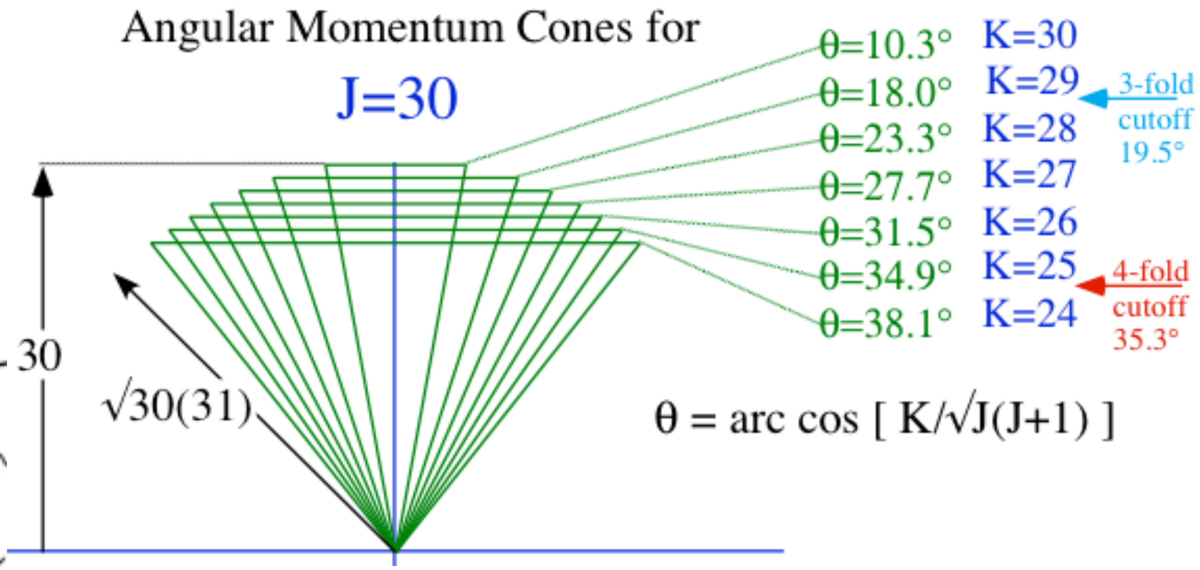
(next page shows slice)

Review: Spherical rotor levels



Review: Spherical rotor levels and spectra





Angular Momentum Cones for

J=30

θ	K
θ=10.3°	K=30
θ=18.0°	K=29
θ=23.3°	K=28
θ=27.7°	K=27
θ=31.5°	K=26
θ=34.9°	K=25
θ=38.1°	K=24

3-fold cutoff 19.5°

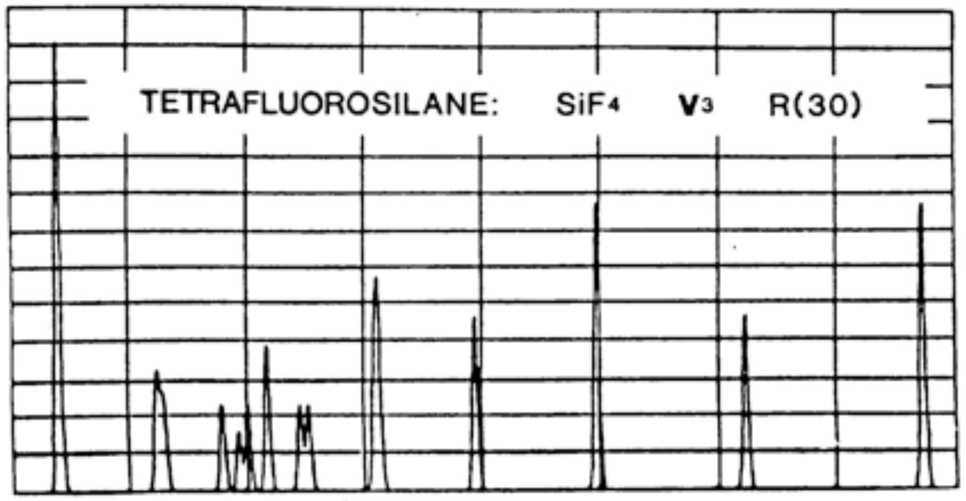
4-fold cutoff 35.3°

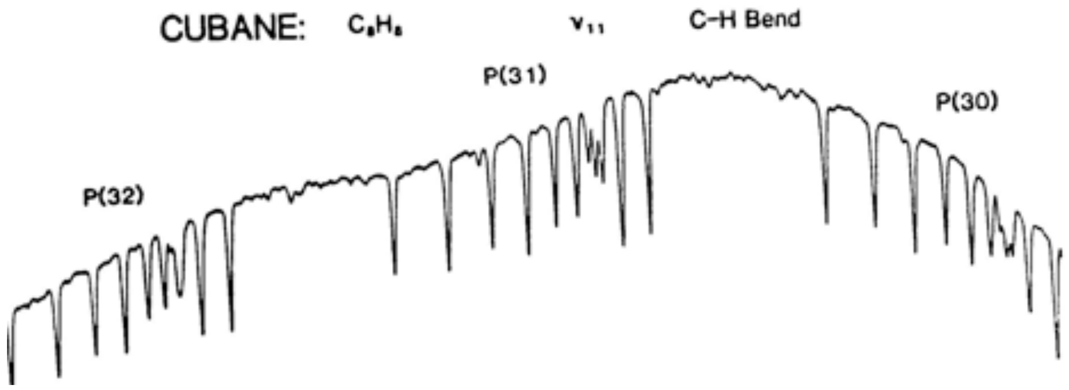
30

$\sqrt{30(31)}$

$\theta = \arccos\left[K/\sqrt{J(J+1)} \right]$

Two molecular examples: SiF_4 and C_8H_8





Review: Spherical rotor levels and RES plots

Spectral fine structure of SF_6, SiF_4, C_8H_8,...

➡ $O\supset C_4$ *and* $O\supset C_3$ *symmetry correlation*

Some more examples of $J=30$ *levels (including* $\mathbf{T}^{[6]}$ *vs* $\mathbf{T}^{[4]}$ *effects)*

Octahedral $O \supset C_4$ subgroup correlations

$\chi^{\mu}_{g}(O)$	$\mathbf{g=1}$	$\mathbf{r}_{1...4}$	180° $\boldsymbol{\rho}_{xyz}$	90° $\mathbf{R}_{xyz}$	180° $\mathbf{i}_{1...6}$
A_1	1	~~1~~	1	1	~~1~~
A_2	1	~~1~~	1	−1	~~−1~~
E	2	~~−1~~	2	0	~~0~~
T_1	3	~~0~~	−1	1	~~−1~~
T_2	3	~~0~~	−1	−1	~~1~~

$\chi^{\mu}_{g}(C_4)$	$\mathbf{g=1}$	$\mathbf{R}_{z+90°}$	$\mathbf{R}_{z+180°}$	$\mathbf{R}_{z-90°}$
$(0)_4$	1	1	1	1
$(1)_4$	1	i	−1	$-i$
$(2)_4$	1	−1	1	−1
$(3)_4$	1	$-i$	−1	i

$\mathbf{1},\ \mathbf{R}_{z+90°},\ \boldsymbol{\rho}_{z180°},\ \mathbf{R}_{z-90°}$

$A_1(O)\downarrow C_4 = 1,\ 1,\ 1,\ 1. \quad =(0)_4$

$A_2(O)\downarrow C_4 = 1,\ -1,\ 1,\ -1. \quad =(2)_4$

$E(O)\downarrow C_4 = 2,\ 0,\ 2,\ 0. \quad =(0)_4 \oplus (2)_4$

$T_1(O)\downarrow C_4 = 3,\ 1,\ -1,\ 1. \quad =(0)_4 \oplus (1)_4 \oplus (3)_4$

$T_2(O)\downarrow C_4 = 3,\ -1,\ -1,\ -1. \quad =(2)_4 \oplus (1)_4 \oplus (3)_4$

$O\downarrow C_4$ subduction

$O\downarrow C_4$	0_4	1_4	2_4	$3_4 = \bar{1}_4$
A_1	1	·	·	·
A_2	·	·	1	·
E	1	·	1	·
T_1	1	1	·	1
T_2	·	1	1	1

Octahedral $O \supset C_3$ subgroup correlations

$\chi^{\mu}_{g}(O)$	$\mathbf{g=1}$	$\mathbf{r}_{1...4}$	$\boldsymbol{\rho}_{xyz}$	$\mathbf{R}_{xyz}$	$\mathbf{i}_{1...6}$
A_1	1	1	~~1~~	~~1~~	~~1~~
A_2	1	1	~~1~~	~~−1~~	~~−1~~
E	2	−1	~~2~~	~~0~~	~~0~~
T_1	3	0	~~−1~~	~~1~~	~~−1~~
T_2	3	0	~~−1~~	~~−1~~	~~1~~

$\chi^{\mu}_{g}(C_3)$	$\mathbf{g=1}$	$r_{z+120°}$	$r_{z-120°}$
$(0)_3$	1	1	1
$(1)_3$	1	$e^{i2\pi/3}$	$e^{-i2\pi/3}$
$(2)_3$	1	$e^{-i2\pi/3}$	$e^{i2\pi/3}$

$\mathbf{1},\ \mathbf{r}_{z+120°},\ \mathbf{r}_{z-120°},\ \mathbf{R}_{z-90°}$

$A_1(O)\downarrow C_3 = 1,\ 1,\ 1. \quad =(0)_3$

$A_2(O)\downarrow C_3 = 1,\ 1,\ 1. \quad =(0)_3$

$E(O)\downarrow C_3 = 2,\ -1,\ -1. \quad =(1)_3 \oplus (3)_3$

$T_1(O)\downarrow C_3 = 3,\ 0,\ 0. \quad =(0)_3 \oplus (1)_3 \oplus (3)_3$

$T_2(O)\downarrow C_3 = 3,\ 0,\ 0. \quad =(0)_3 \oplus (1)_3 \oplus (3)_3$

$O\downarrow C_3$ subduction

$O\downarrow C_3$	0_3	1_3	$2_3 = \bar{1}_3$
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

Review: Spherical rotor levels and RES plots

Spectral fine structure of SF_6, SiF_4, C_8H_8,...

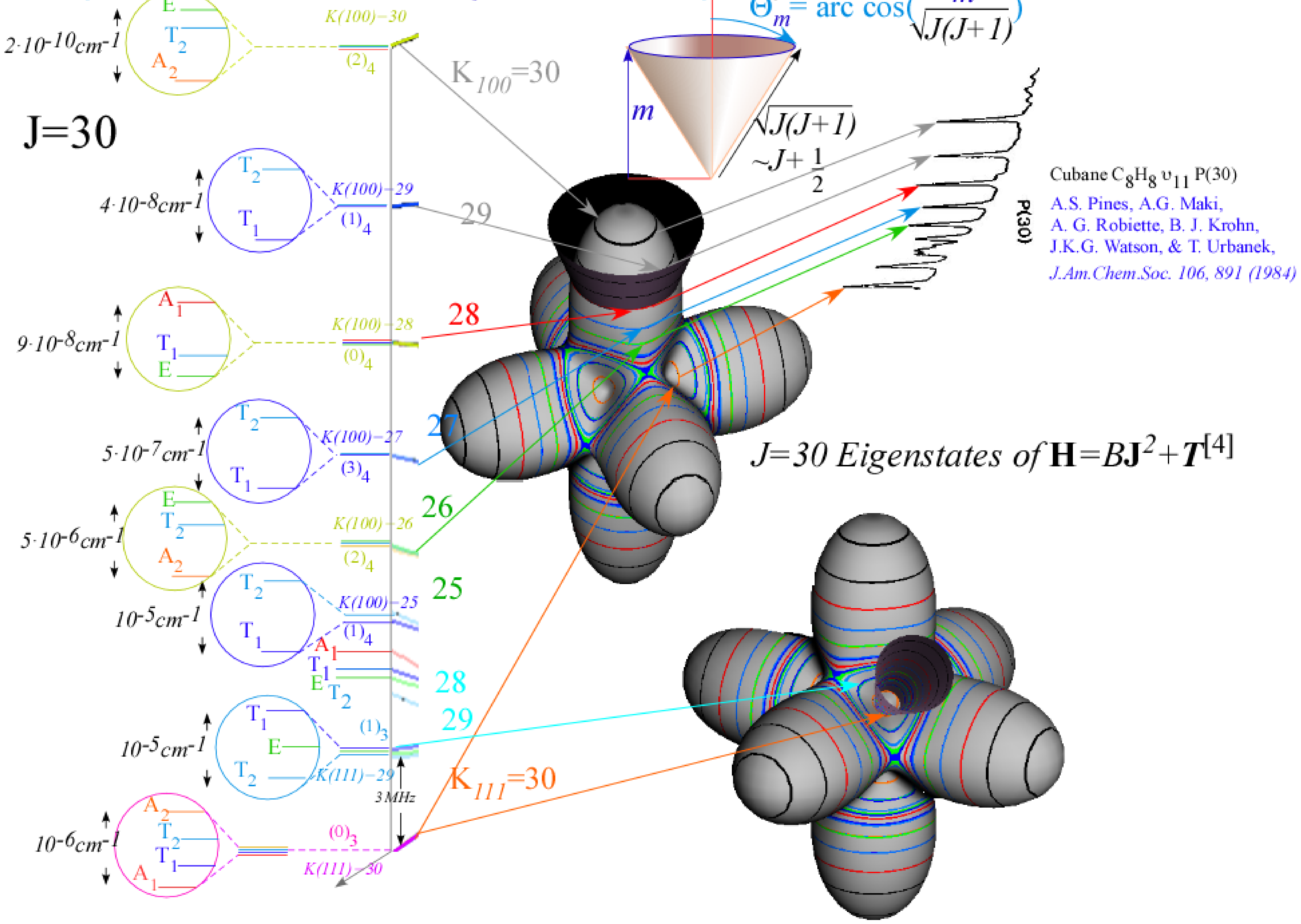
$O \supset C_4$ and $O \supset C_3$ symmetry correlation

➡ *Some more examples of J=30 levels (including* $\mathbf{T}^{[6]}$ *vs* $\mathbf{T}^{[4]}$ *effects)*

Angular Momentum Cones and Quantum Polar Angles

$$\Theta^J_m = \arccos\left(\frac{m}{\sqrt{J(J+1)}}\right)$$

J=30



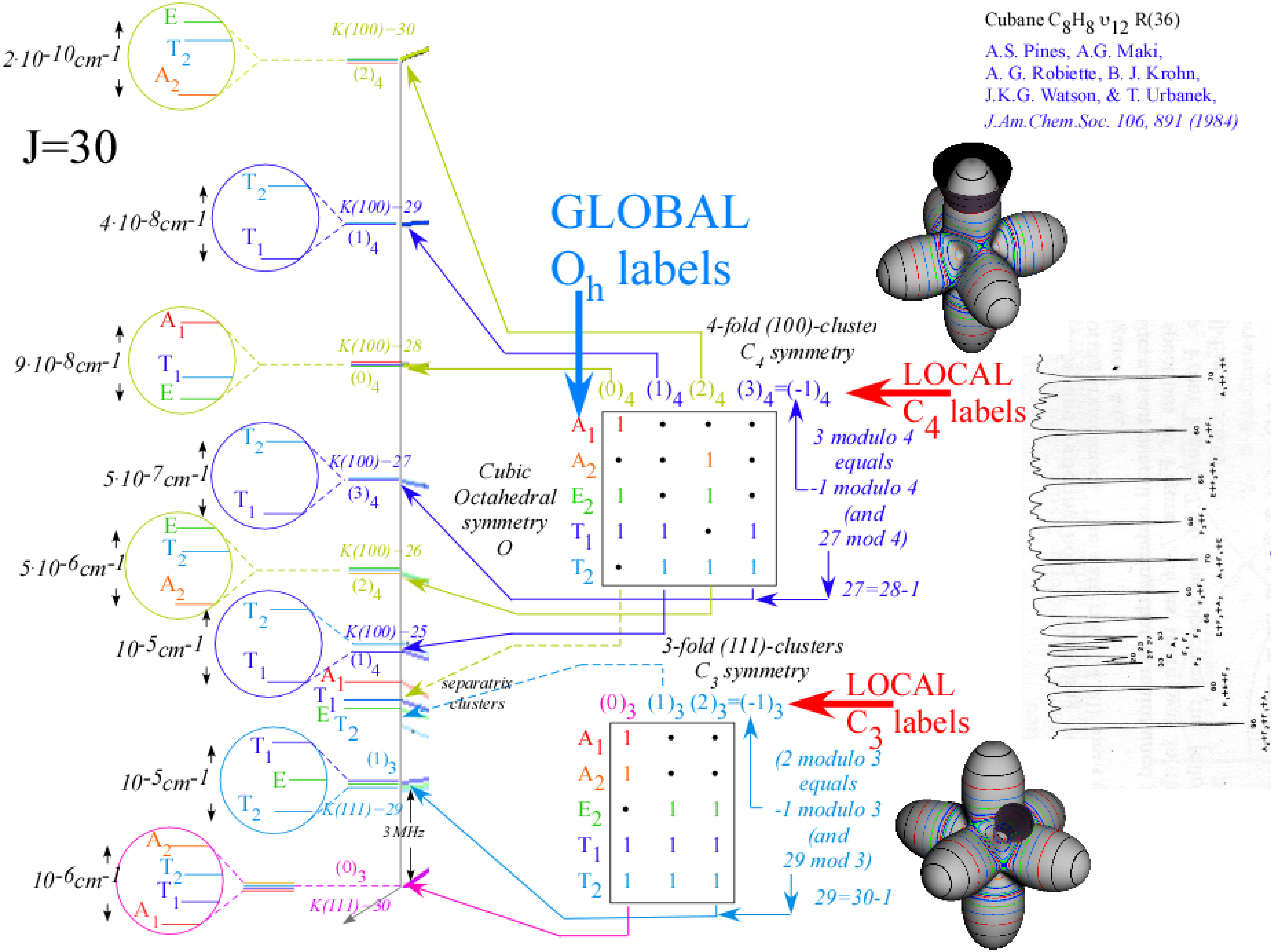
Cubane C_8H_8 υ_{11} P(30)

A.S. Pines, A.G. Maki,
A. G. Robiette, B. J. Krohn,
J.K.G. Watson, & T. Urbanek,
J.Am.Chem.Soc. 106, 891 (1984)

J=30 Eigenstates of $\mathbf{H}=B\mathbf{J}^2+T^{[4]}$

Review: *Spherical rotor levels and spectra*

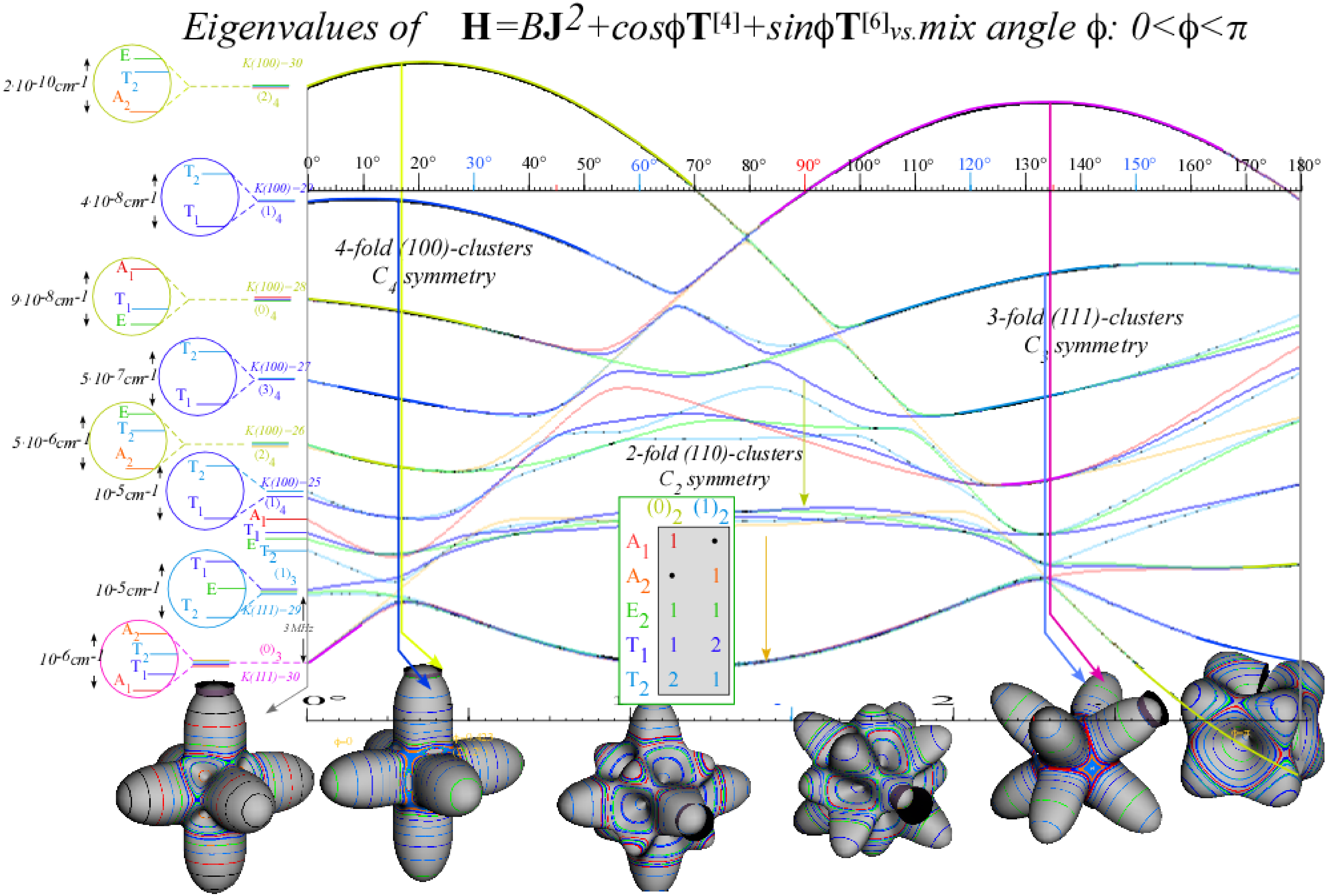
Cubane C_8H_8 υ_{12} R(36)
A.S. Pines, A.G. Maki,
A. G. Robiette, B. J. Krohn,
J.K.G. Watson, & T. Urbanek,
J.Am.Chem.Soc. 106, 891 (1984)



	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E_2	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

	$(0)_3$	$(1)_3$	$(2)_3=(-1)_3$
A_1	1	•	•
A_2	1	•	•
E_2	•	1	1
T_1	1	1	1
T_2	1	1	1

Review: Spherical rotor level $T^{[4]}+T^{[6]}$ *Tensor eigenlevels*



Eigenvalues of $\mathbf{H}=B\mathbf{J}^2+\cos\phi\,\mathbf{T}^{[4]}+\sin\phi\,\mathbf{T}^{[6]}$ vs. mix angle ϕ: $0<\phi<\pi$

	$(0)_2$	$(1)_2$
A_1	1	•
A_2	•	1
E_2	1	1
T_1	1	2
T_2	2	1

after: Int.J.Molecular Science 14.(2013) Fig.6 p.742 and Fig. 29 p.791

Details of P(88) v_4 SF_6 and P(88) v_4 CF_4 spectral structure and implications

- ➡ *Outline of rovibronic Hamiltonian theory*
    - *Coriolis scalar interaction*
- *Rovibronic nomograms and PQR structure*
- *Rovibronic energy surfaces (RES) and cone geometry*
- *Spin symmetry correlation, tunneling, and entanglement*
    - *Hyperfine vs. superfine structure (Case 1. vs Case 2.)*
    - *Spin-0 nuclei give Bose Exclusion*
        - *The spin-symmetry species mixing problem*
- *Analogy between PE surface dynamics and RES*
- *Rotational Energy Eigenvalue Surfaces (REES)*

Symmetry-level-cluster effects in SF_6, SiF_4, CH_4, CF_4
Graphical approach to rotation-vibration-spin Hamiltonian

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

to help understand complex rotational spectra and dynamics.

<u>OUTLINE</u>

Example(s)

Introductory review

- *Rovibronic nomograms and PQR structure* — ν_3 and ν_4 SF_6
- *Rotational Energy Surfaces (RES) and θ^J_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

$\nu_3/2\nu_4$

Details of P(88) v_4 SF_6 and P(88) v_4 CF_4 spectral structure and implications

- *Outline of rovibronic Hamiltonian theory*
  - ➡ *Coriolis scalar interaction*
- *Rovibronic nomograms and PQR structure*
- *Rovibronic energy surfaces (RES) and cone geometry*
- *Spin symmetry correlation, tunneling, and entanglement*
  - *Hyperfine vs. superfine structure (Case 1. vs Case 2.)*
  - *Spin-0 nuclei give Bose Exclusion*
    - *The spin-symmetry species mixing problem*
- *Analogy between PE surface dynamics and RES*
- *Rotational Energy Eigenvalue Surfaces (REES)*

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

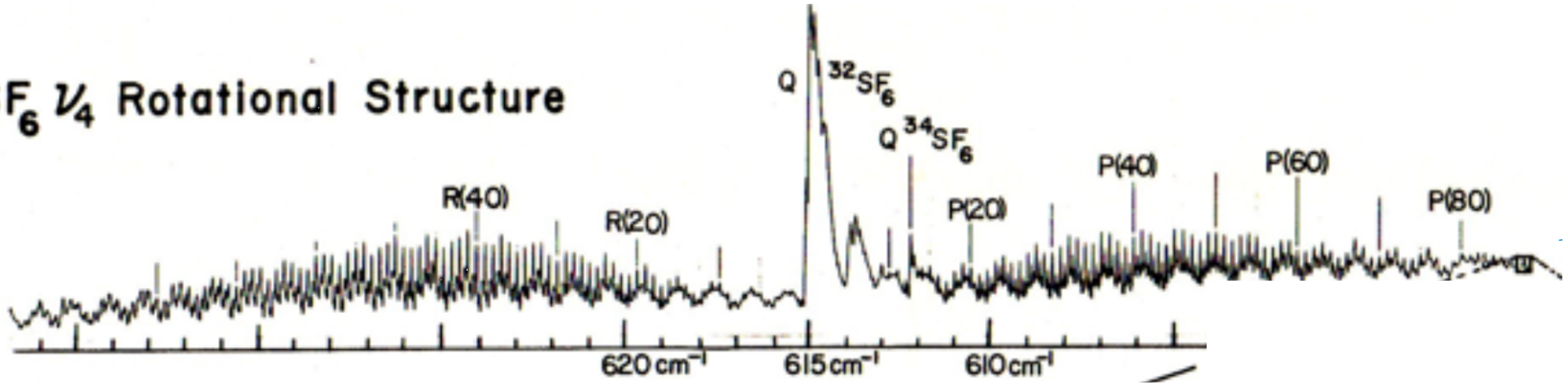
Introductory review

Example(s)

- *Rovibronic nomograms and PQR structure* — ν_3 and ν_4 SF_6
- *Rotational Energy Surfaces (RES) and Θ^{ℓ}_{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



(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).

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

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

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

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

$$= -B\zeta\,[\,J(J+1)-N(N+1)+\ell(\ell+1)]$$

Involves:

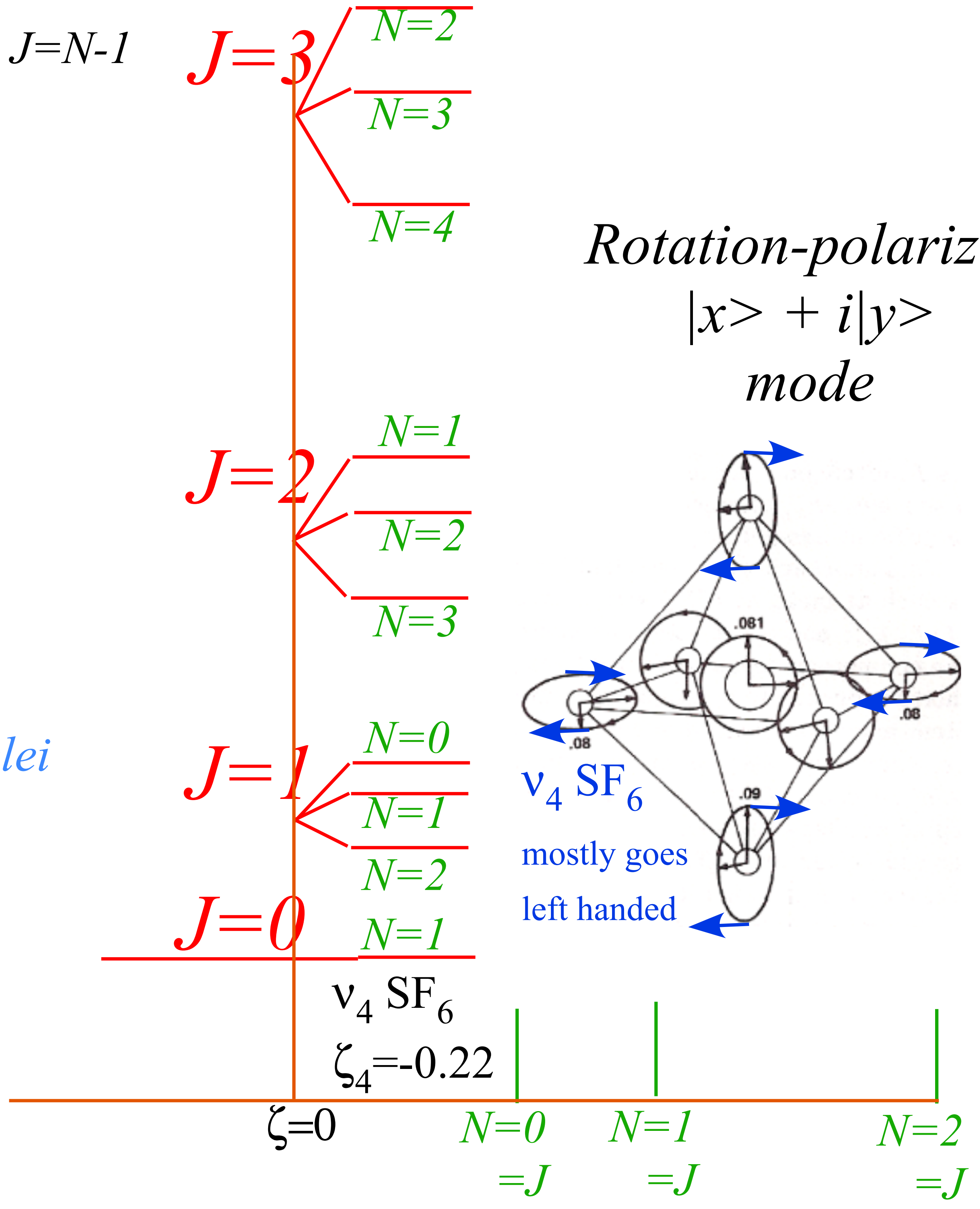
angular momentum ℓ of vibration “orbits”

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

total momentum **J** *=ℓ+***N** *of whole molecule.*

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

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



Rotation-polarized
|x> + i|y>
mode

ν_4 SF$_6$
mostly goes
left handed

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

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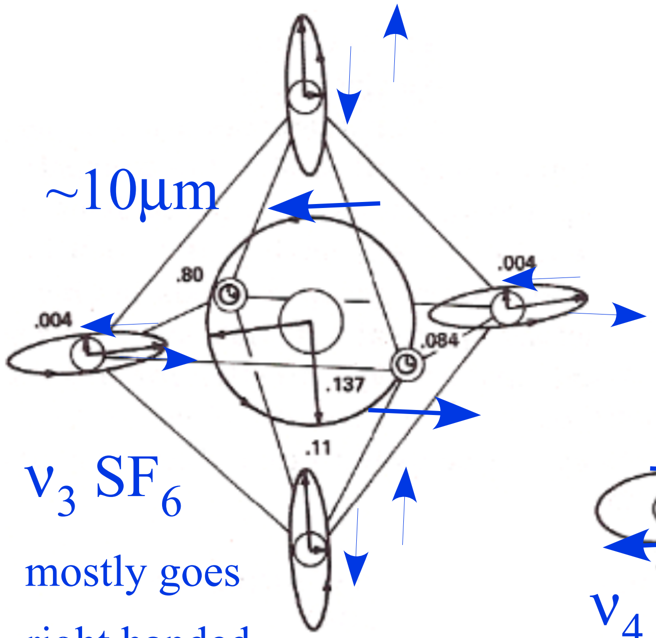
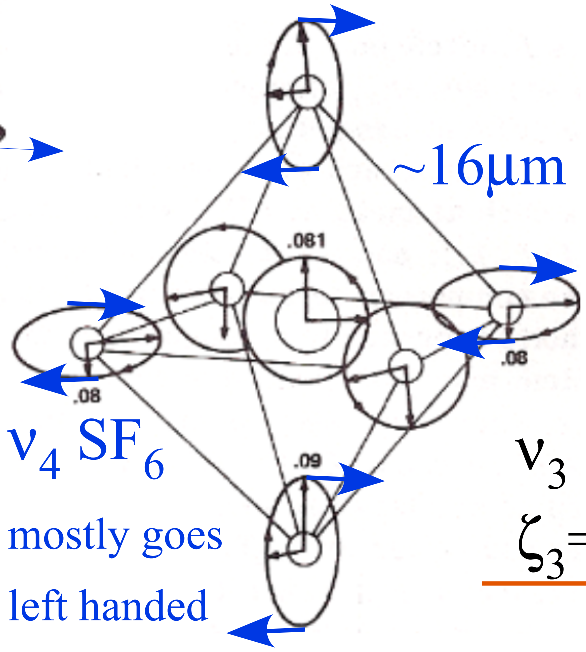


~10μm

ν_3 SF$_6$

mostly goes

right handed

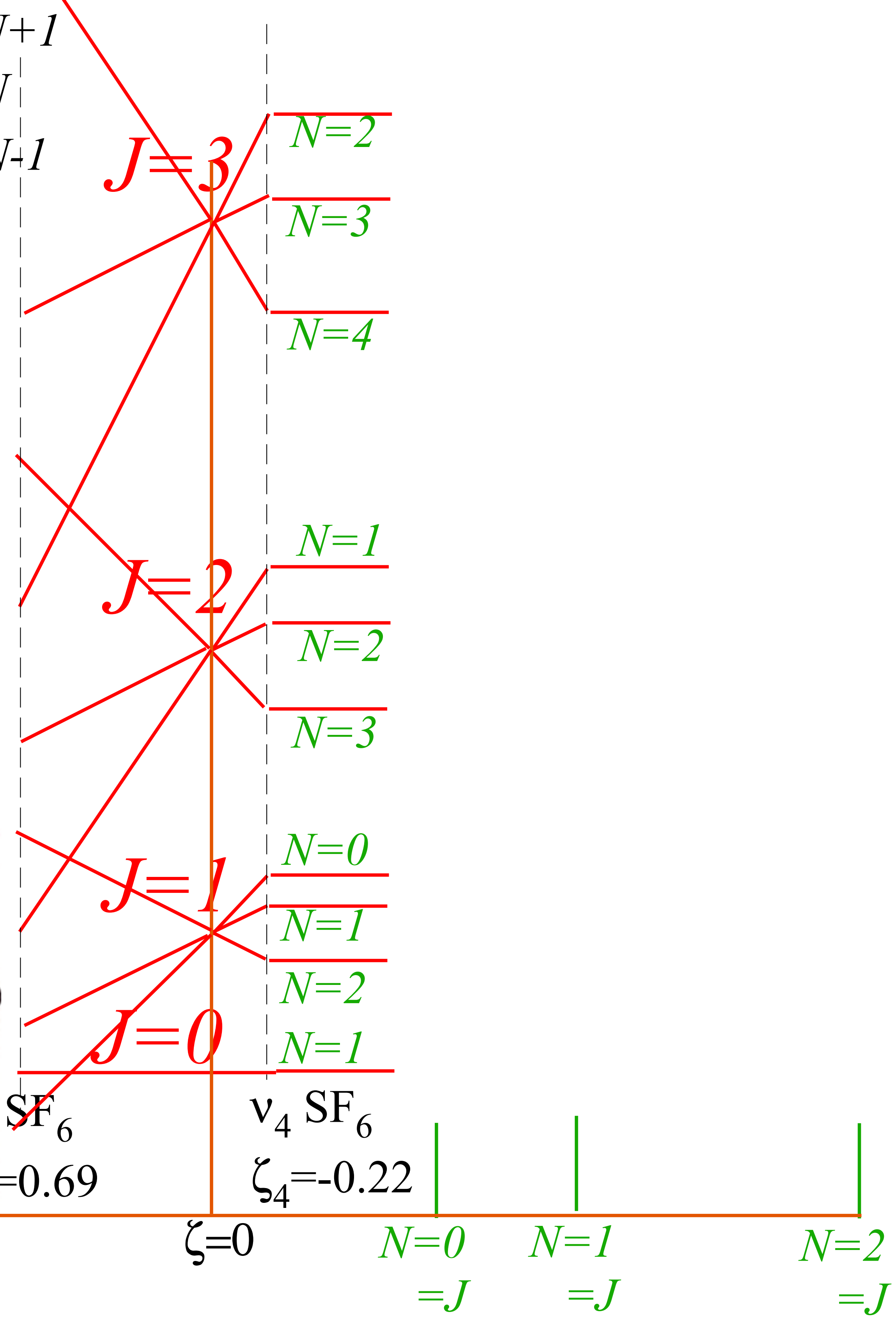


~16μm

ν_4 SF$_6$

mostly goes

left handed



Details of $P(88)$ v_4 SF_6 and $P(88)$ v_4 CF_4 spectral structure and implications

- *Outline of rovibronic Hamiltonian theory*
  - *Coriolis scalar interaction*
- ➡ *Rovibronic nomograms and PQR structure*
- *Rovibronic energy surfaces (RES) and cone geometry*
- *Spin symmetry correlation, tunneling, and entanglement*
  - *Hyperfine vs. superfine structure (Case 1. vs Case 2.)*
  - *Spin-0 nuclei give Bose Exclusion*
    - *The spin-symmetry species mixing problem*
- *Analogy between PE surface dynamics and RES*
- *Rotational Energy Eigenvalue Surfaces (REES)*

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

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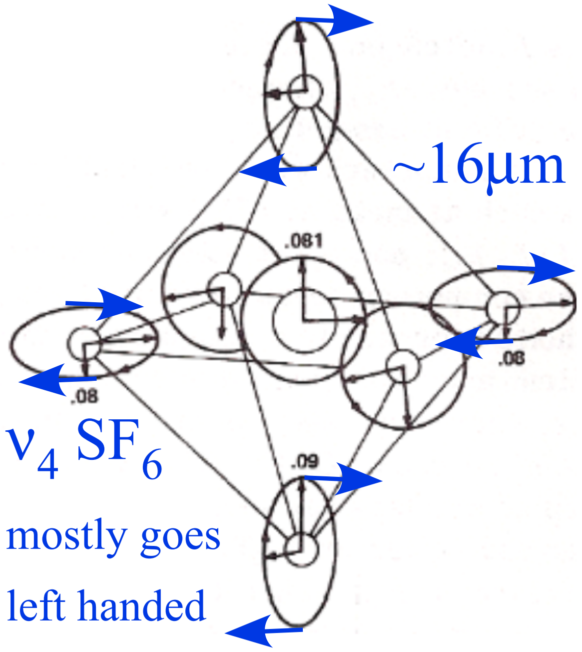
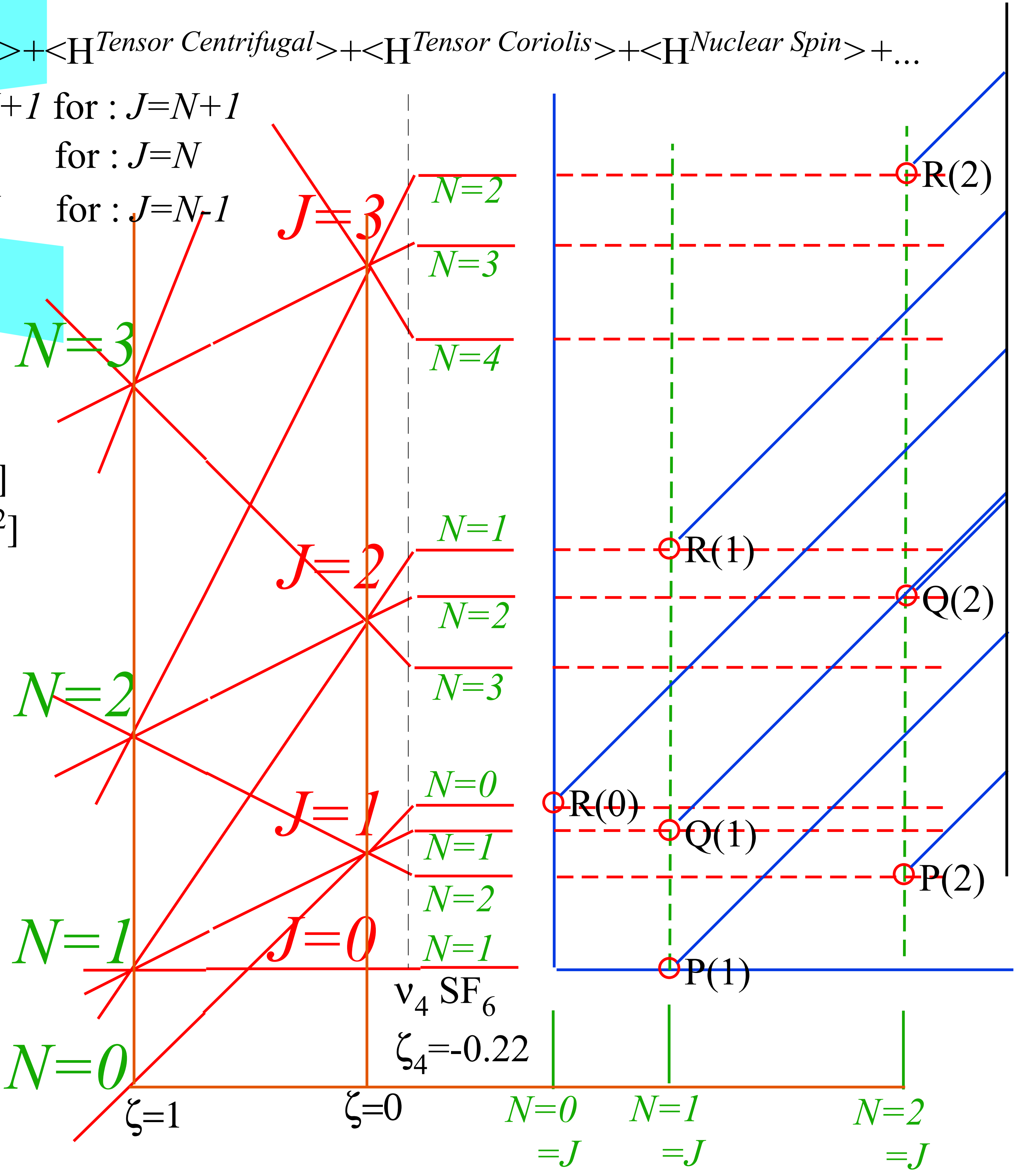
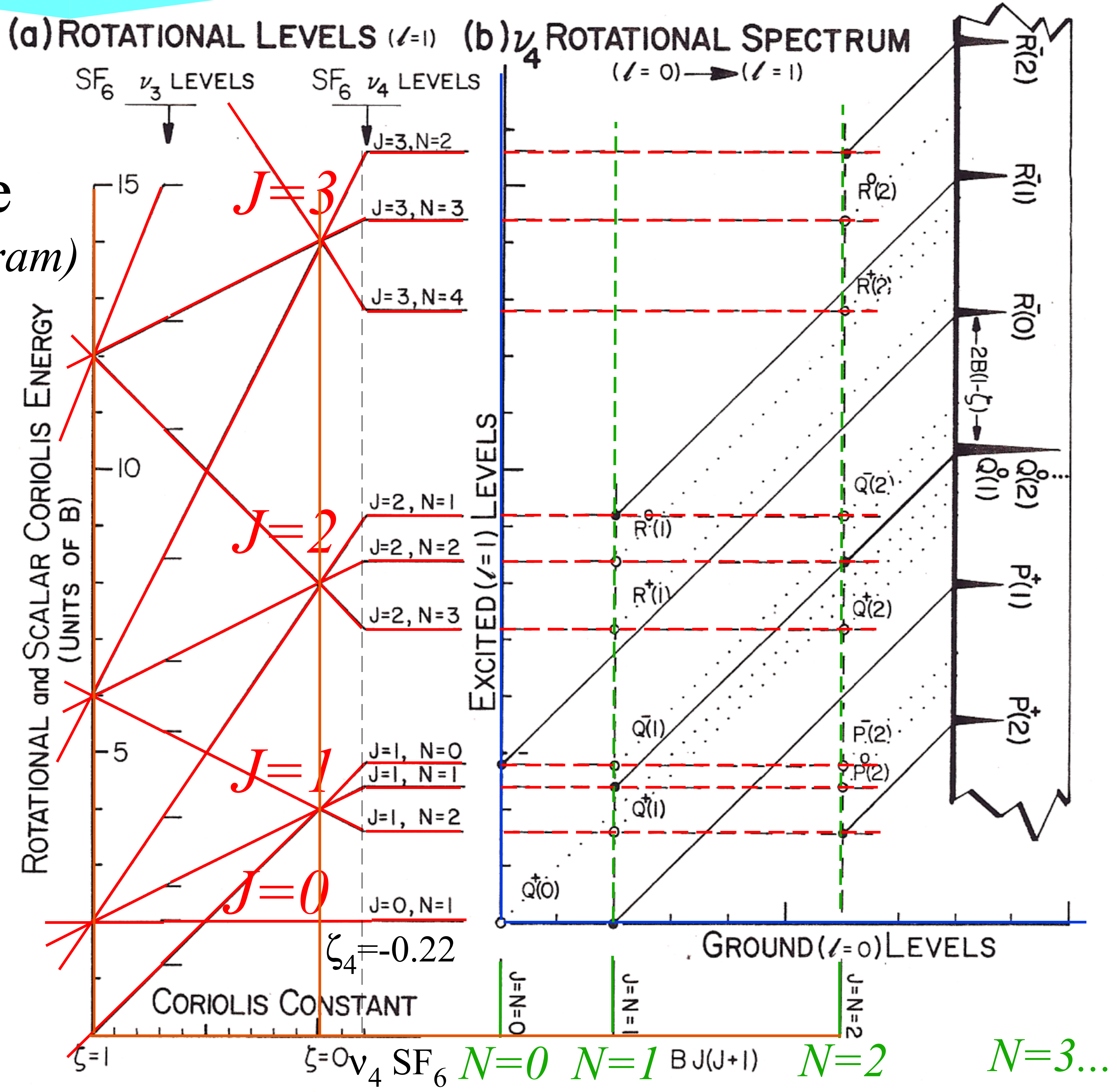


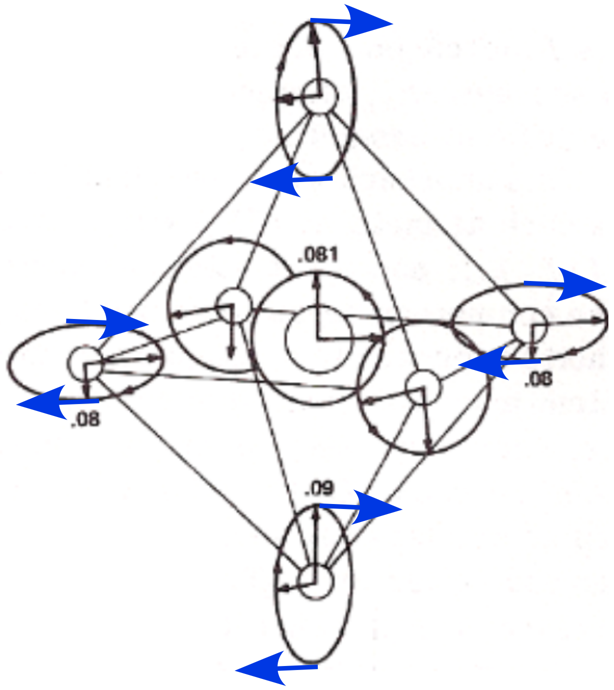


$$\langle H\rangle \sim \nu_{vib}+BJ(J+1)+\langle H^{Scalar\ Coriolis}\rangle+\langle H^{Tensor\ Centrifugal}\rangle+\langle H^{Tensor\ Coriolis}\rangle+\langle H^{Nuclear\ Spin}\rangle+\ldots$$

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

(Using rovib. nomogram)





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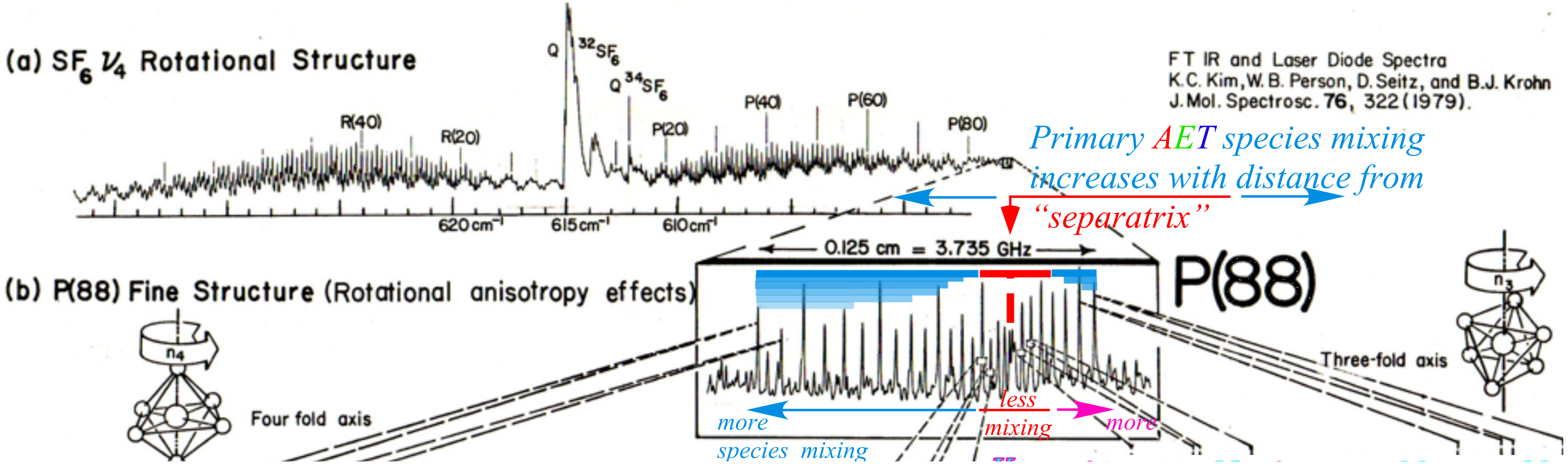

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Primary AET species mixing increases with distance from "separatrix"

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

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

OUTLINE

Introductory review

	Example(s)
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and θ^J_K-cones*	ν_4 P(88) SF_6
• *Spin symmetry correlation tunneling and entanglement*	SF_6

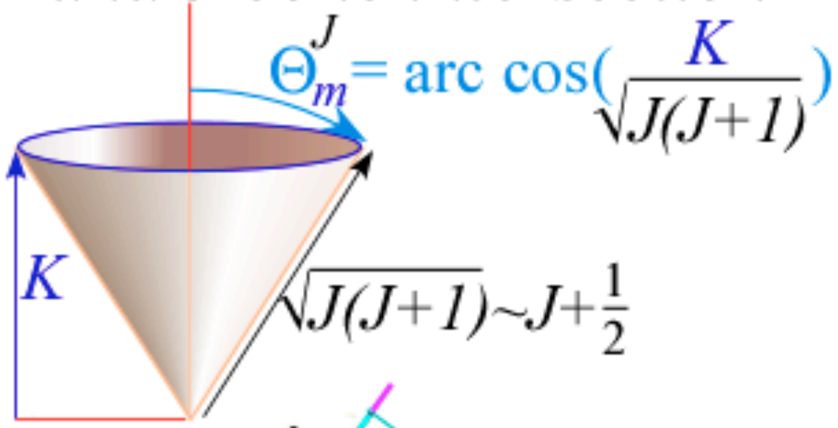
Recent developments

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

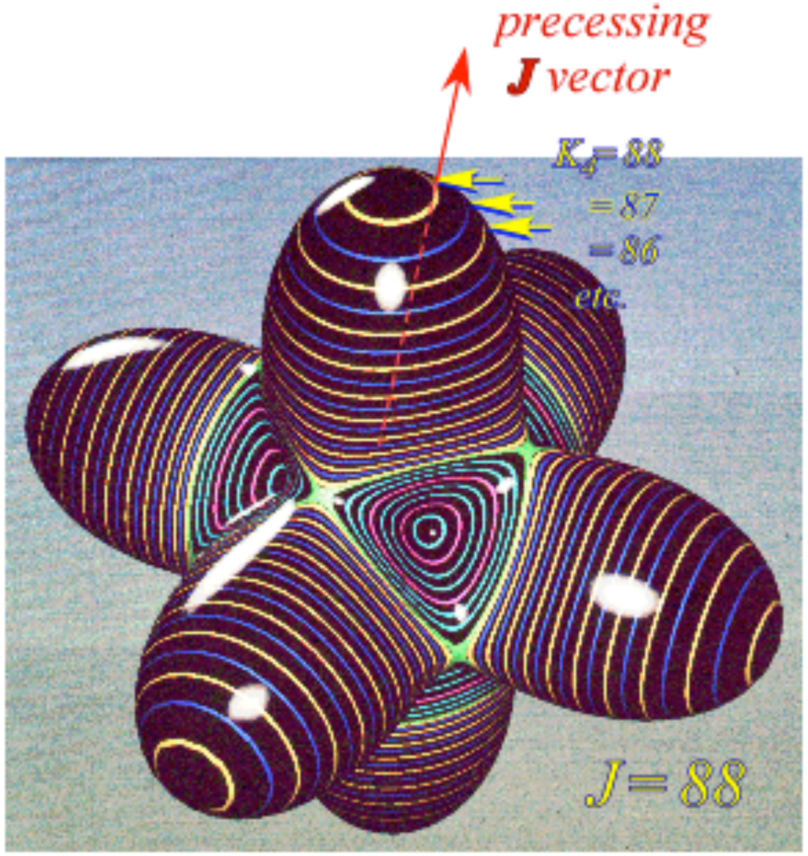
SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography and J-cone intersection

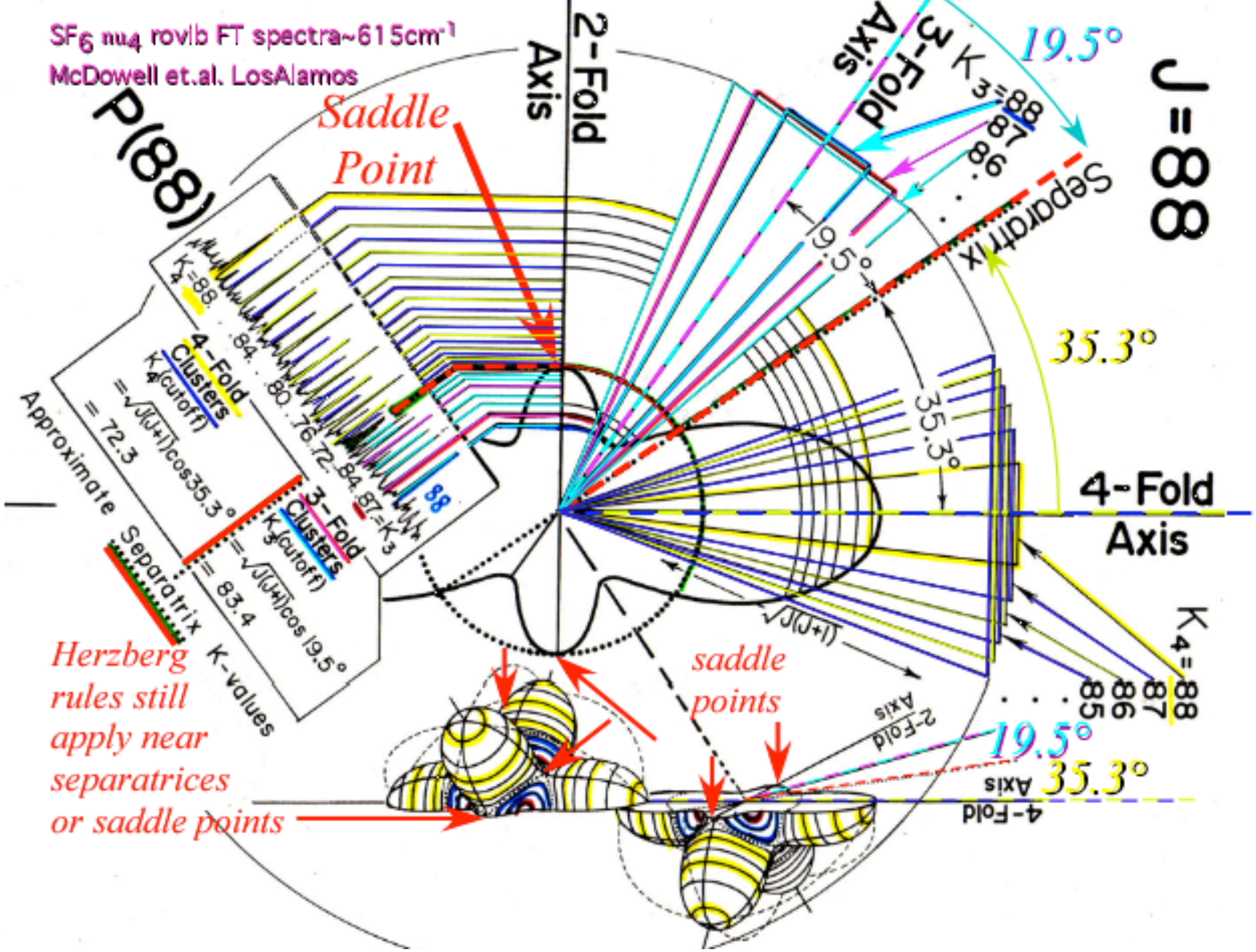
$$\mathbf{H} = B\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right)+t_{440}\left(\mathbf{J}_x^4+\mathbf{J}_y^4+\mathbf{J}_z^4-\frac{3}{5}J^4\right)+\cdots$$

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



Rovibronic Energy (RE) Tensor Surface

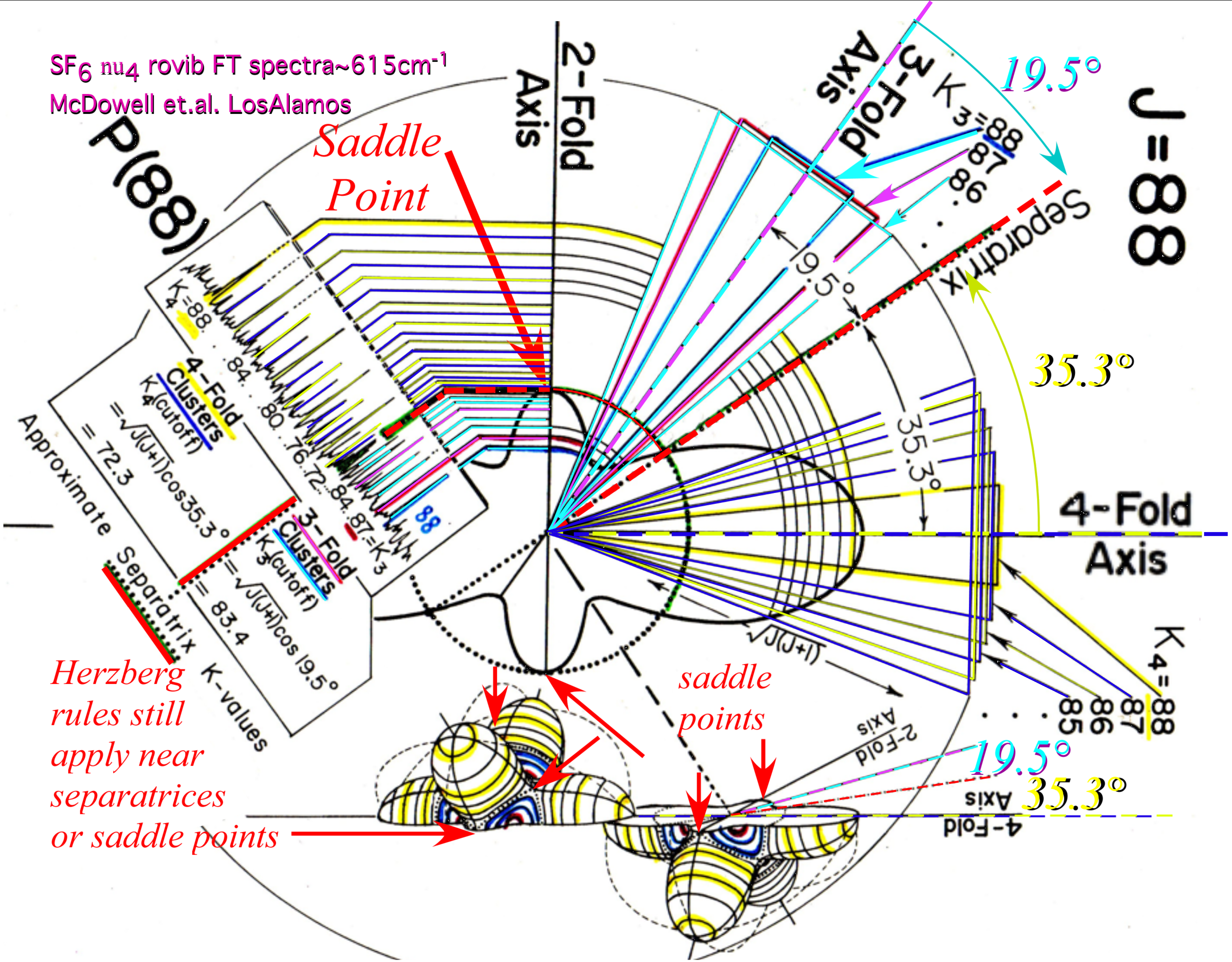




Herzberg rules still apply near separatrices or saddle points

SF$_6$ nu$_4$ rovib FT spectra~615cm^{-1}

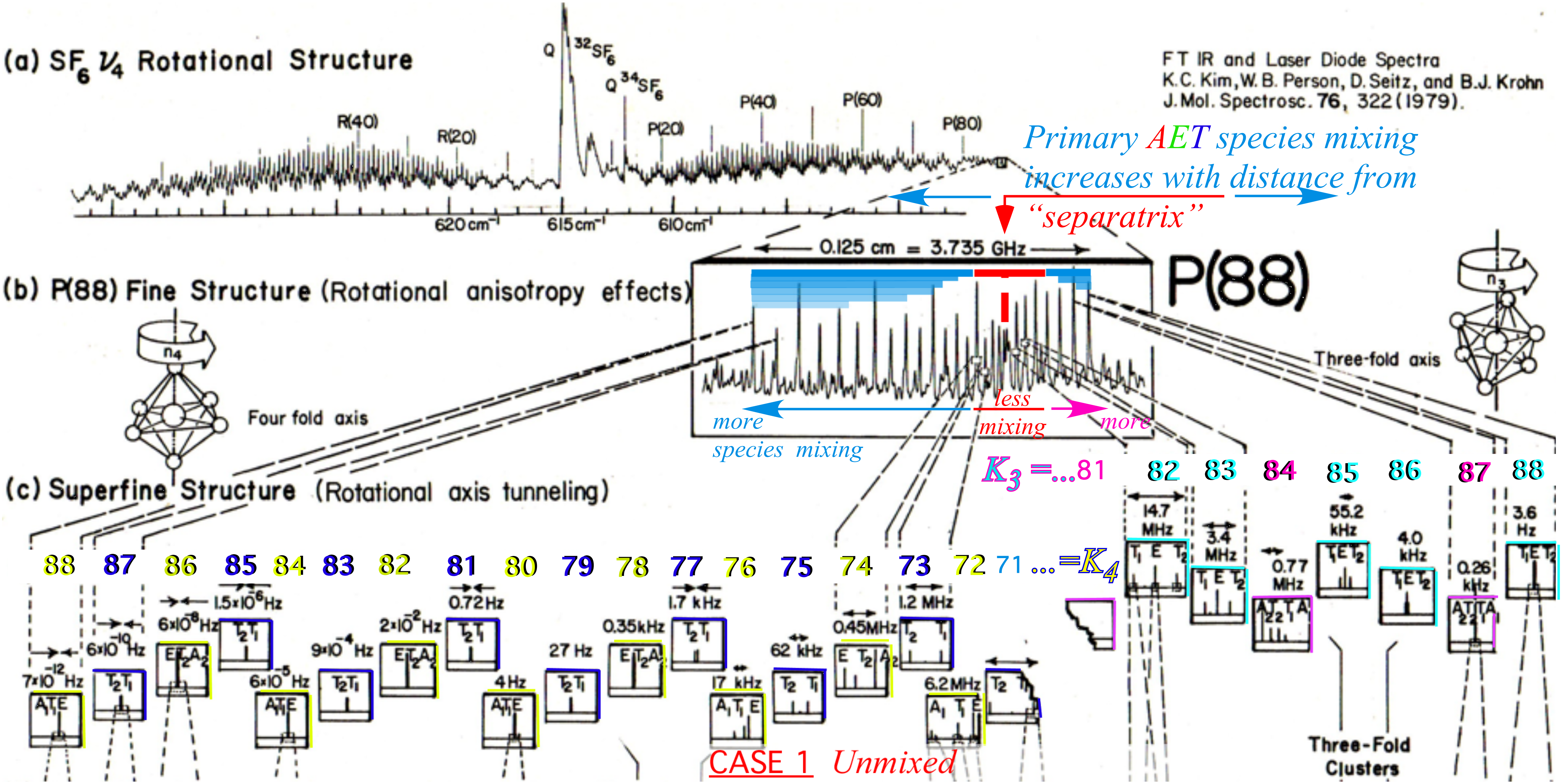
McDowell et.al. LosAlamos



Saddle Point

Herzberg rules still apply near separatrices or saddle points

saddle points



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Primary AET species mixing increases with distance from "separatrix"

more species mixing

less mixing

more

K_3 =...81 82 83 84 85 86 87 88

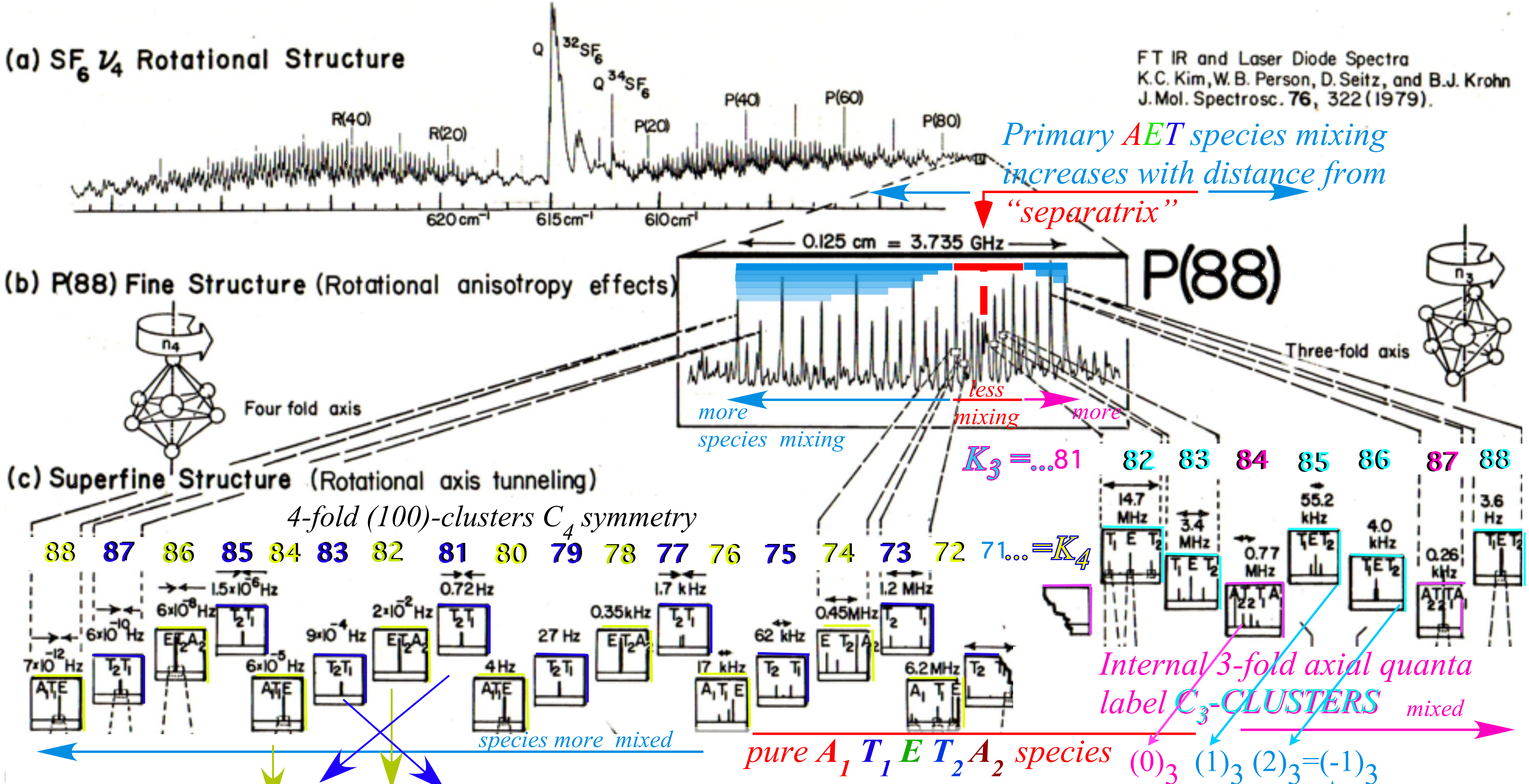
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K_4

CASE 1 *Unmixed*

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.)*



	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

Cubic Octahedral symmetry
O

3 modulo 4 equals -1 modulo 4 (and 83 mod 4)

83=84-1

4-fold (1oo) C_4 symmetry clusters

3-fold (111) C_3 symmetry clusters

	$(0)_3$	$(1)_3$	$(2)_3=(-1)_3$
A_1	1	•	•
A_2	1	•	•
E	•	1	1
T_1	1	1	1
T_2	1	1	1

(2 modulo 3 equals -1 modulo 3 and 86 mod 3)

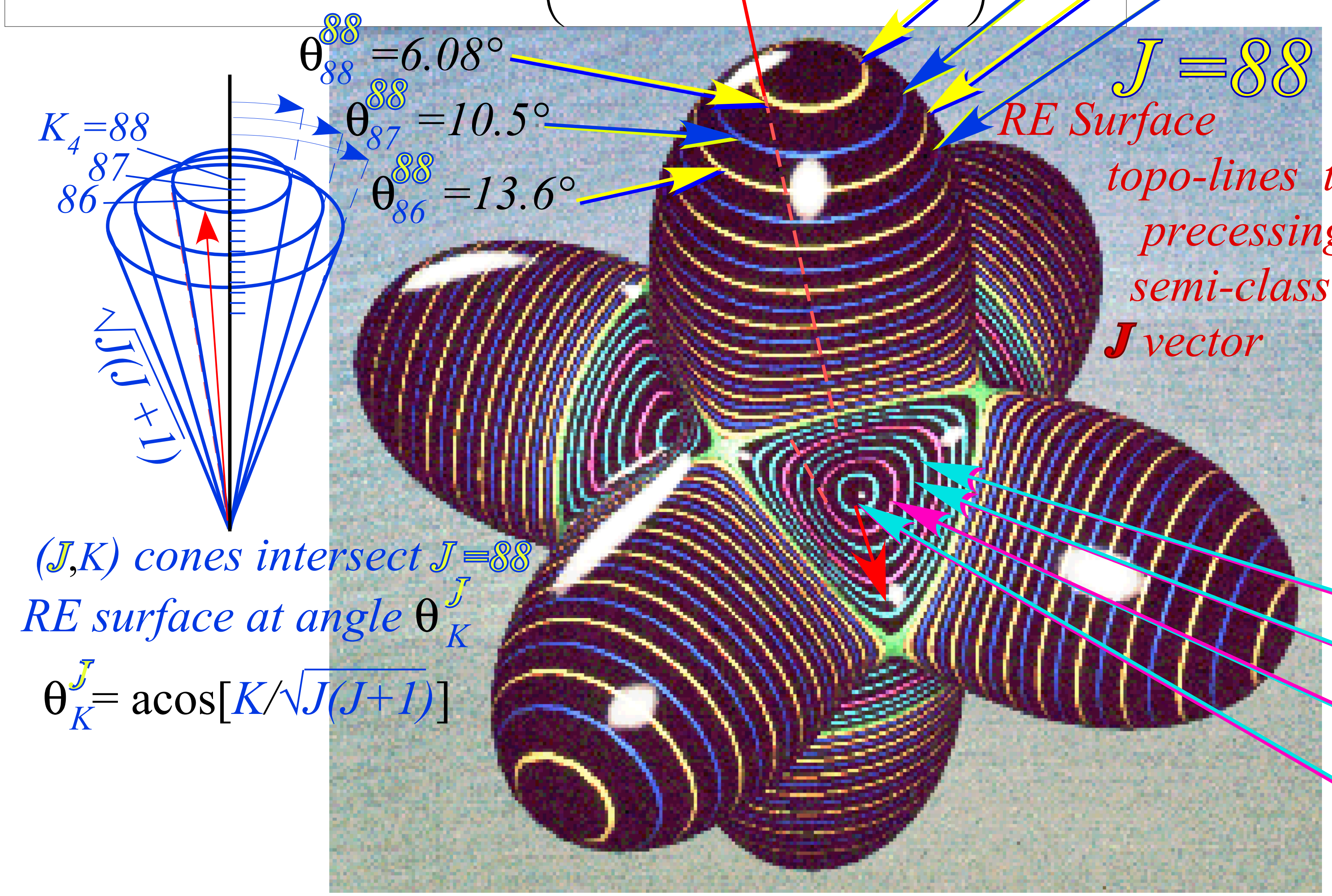
86=88-1

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

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

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

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



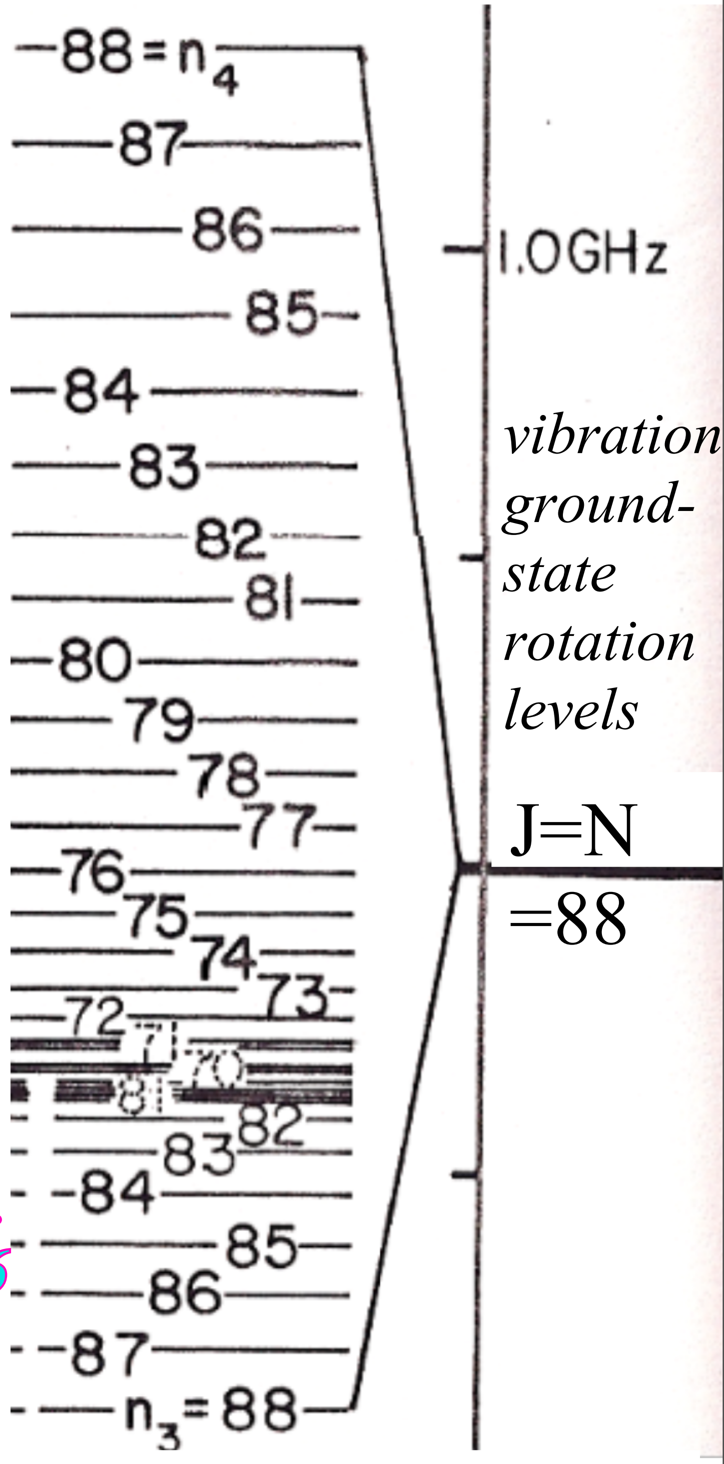
K_4 =88
=87
=87
etc.

*RE Surface topo-lines track precessing semi-classical **J** vector*

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

$$\theta^J_K = \mathrm{acos}[K/\sqrt{J(J+1)}]$$

etc.
=86
=87
K_3 =88



vibration ground-state rotation levels

J=N =88

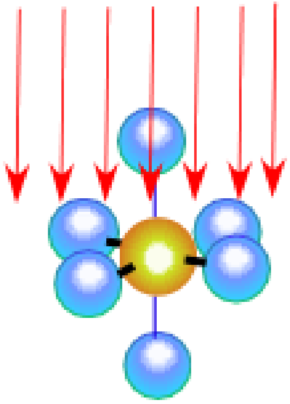
Duality: The "Flip Side" of Symmetry Analysis.

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

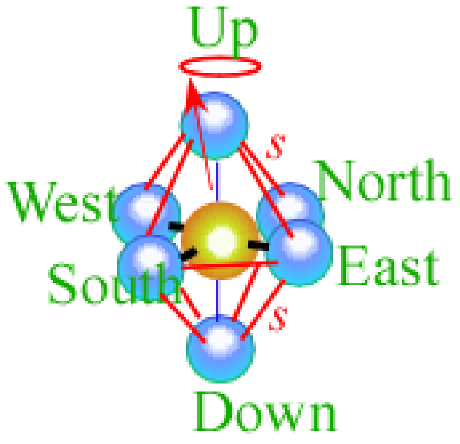


Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

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



$$\begin{array}{cccccc} |U\rangle & |D\rangle & |E\rangle & |W\rangle & |N\rangle & |S\rangle \\ H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{array}$$

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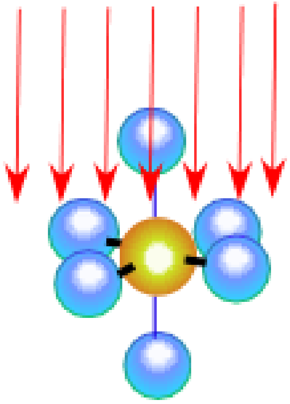
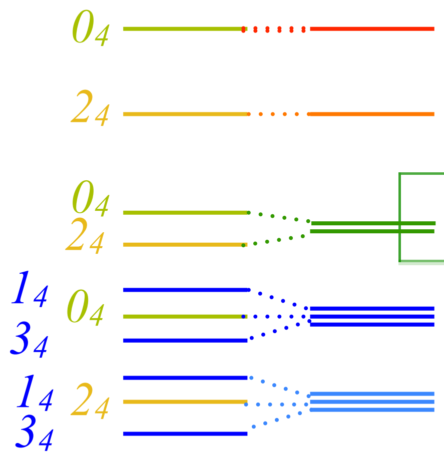
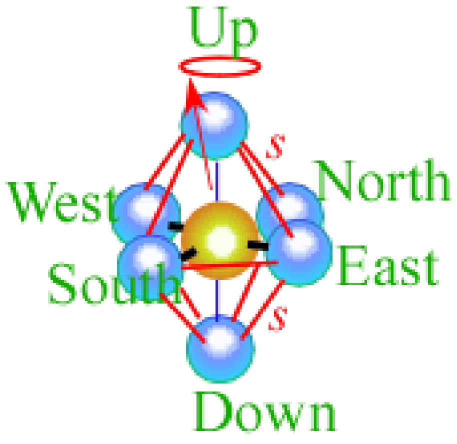




C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1



$$\begin{array}{cccccc} |U\rangle & |D\rangle & |E\rangle & |W\rangle & |N\rangle & |S\rangle \\ H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{array}$$

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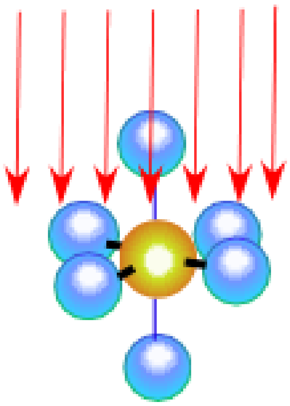
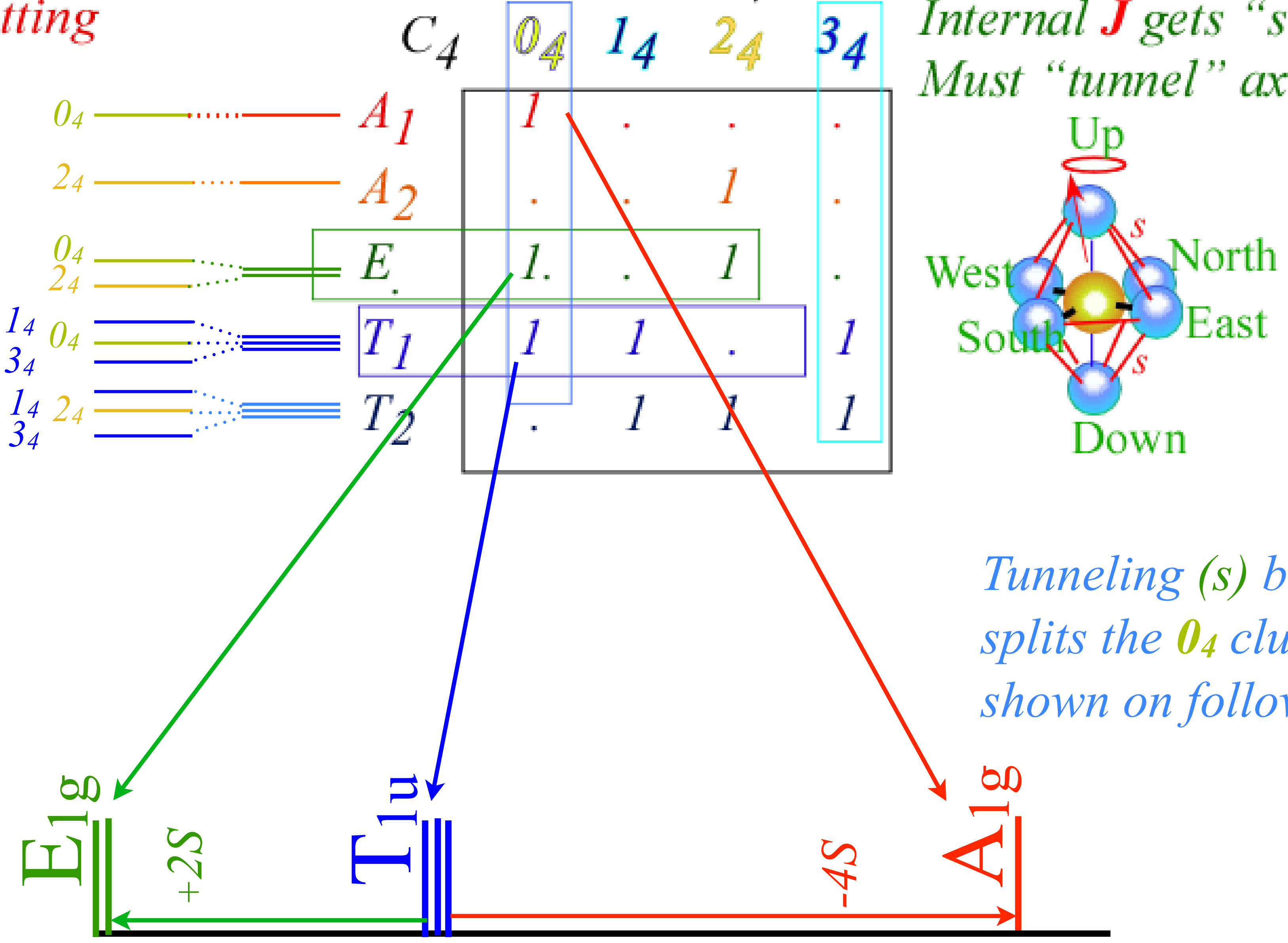




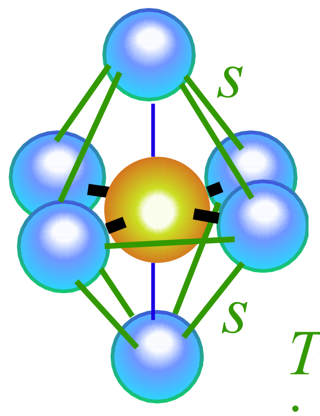
$$
\begin{array}{c|cccc}
C_4 & 0_4 & 1_4 & 2_4 & 3_4 \\
\hline
A_1 & 1 & . & . & . \\
A_2 & . & . & 1 & . \\
E & 1. & . & 1 & . \\
T_1 & 1 & 1 & . & 1 \\
T_2 & . & 1 & 1 & 1
\end{array}
$$

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

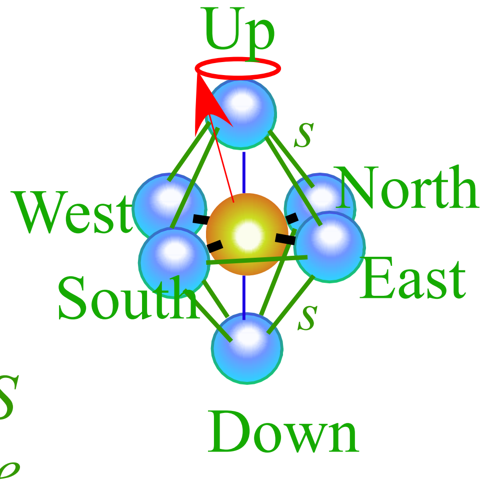
$$
\begin{array}{cccccc}
|U\rangle & |D\rangle & |E\rangle & |W\rangle & |N\rangle & |S\rangle \\
H & 0 & s & s & s & s \\
0 & H & s & s & s & s \\
s & s & H & 0 & s & s \\
s & s & 0 & H & s & s \\
s & s & s & s & H & 0 \\
s & s & s & s & 0 & H
\end{array}
$$

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

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



Tunneling s=-S
is negative here

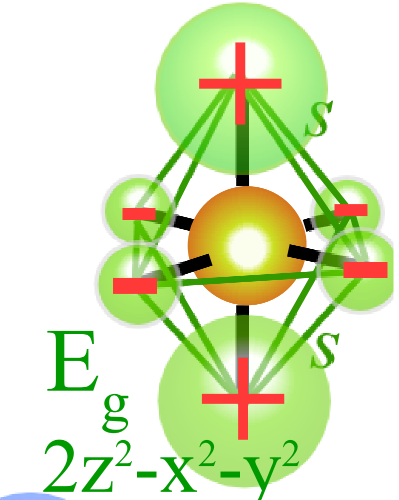


$$\begin{array}{cccccc} |U\rangle & |D\rangle & |E\rangle & |W\rangle & |N\rangle & |S\rangle \\ \hline H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{array}$$

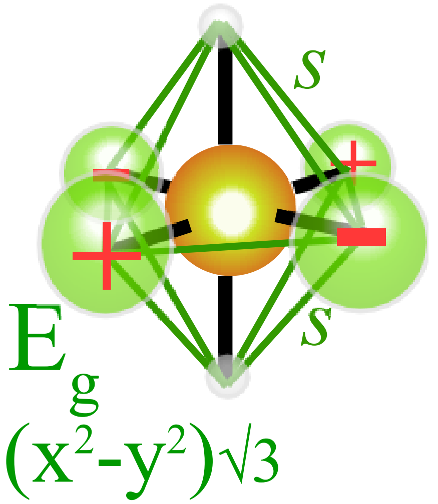
$$\begin{vmatrix} H&0&s&s&s&s\\0&H&s&s&s&s\\s&s&H&0&s&s\\s&s&0&H&s&s\\s&s&s&s&H&0\\s&s&s&s&0&H\end{vmatrix}\begin{vmatrix}+2\\+2\\-1\\-1\\-1\\-1\end{vmatrix}\frac{1}{\sqrt{12}}=(H-2s)\begin{vmatrix}+2\\+2\\-1\\-1\\-1\\-1\end{vmatrix}\frac{1}{\sqrt{12}}$$

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

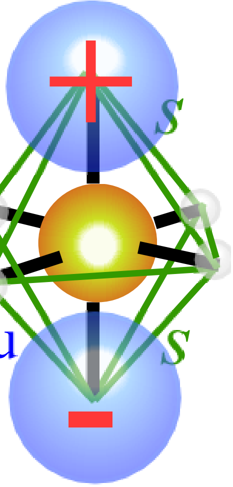
$$\begin{vmatrix} H&0&s&s&s&s\\0&H&s&s&s&s\\s&s&H&0&s&s\\s&s&0&H&s&s\\s&s&s&s&H&0\\s&s&s&s&0&H\end{vmatrix}\begin{vmatrix}1\\1\\1\\1\\1\\1\end{vmatrix}\frac{1}{\sqrt{6}}=(H+4s)\begin{vmatrix}1\\1\\1\\1\\1\\1\end{vmatrix}\frac{1}{\sqrt{6}}$$



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

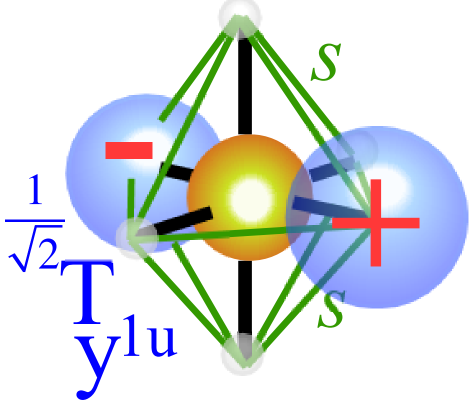


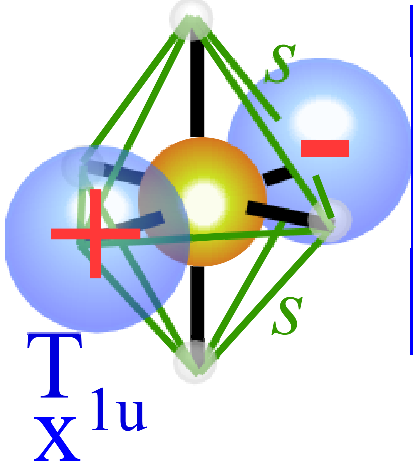
$$\begin{vmatrix}0\\0\\-1\\-1\\+1\\+1\end{vmatrix}\frac{1}{2}$$



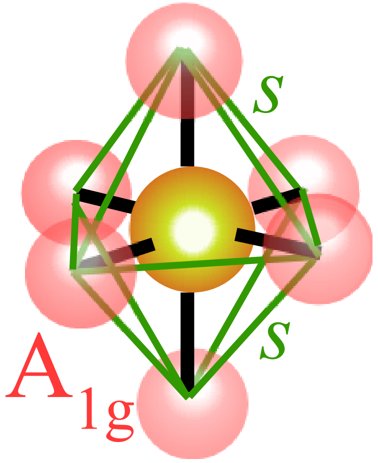
T_{1u} z

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





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



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

Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

boils down to :

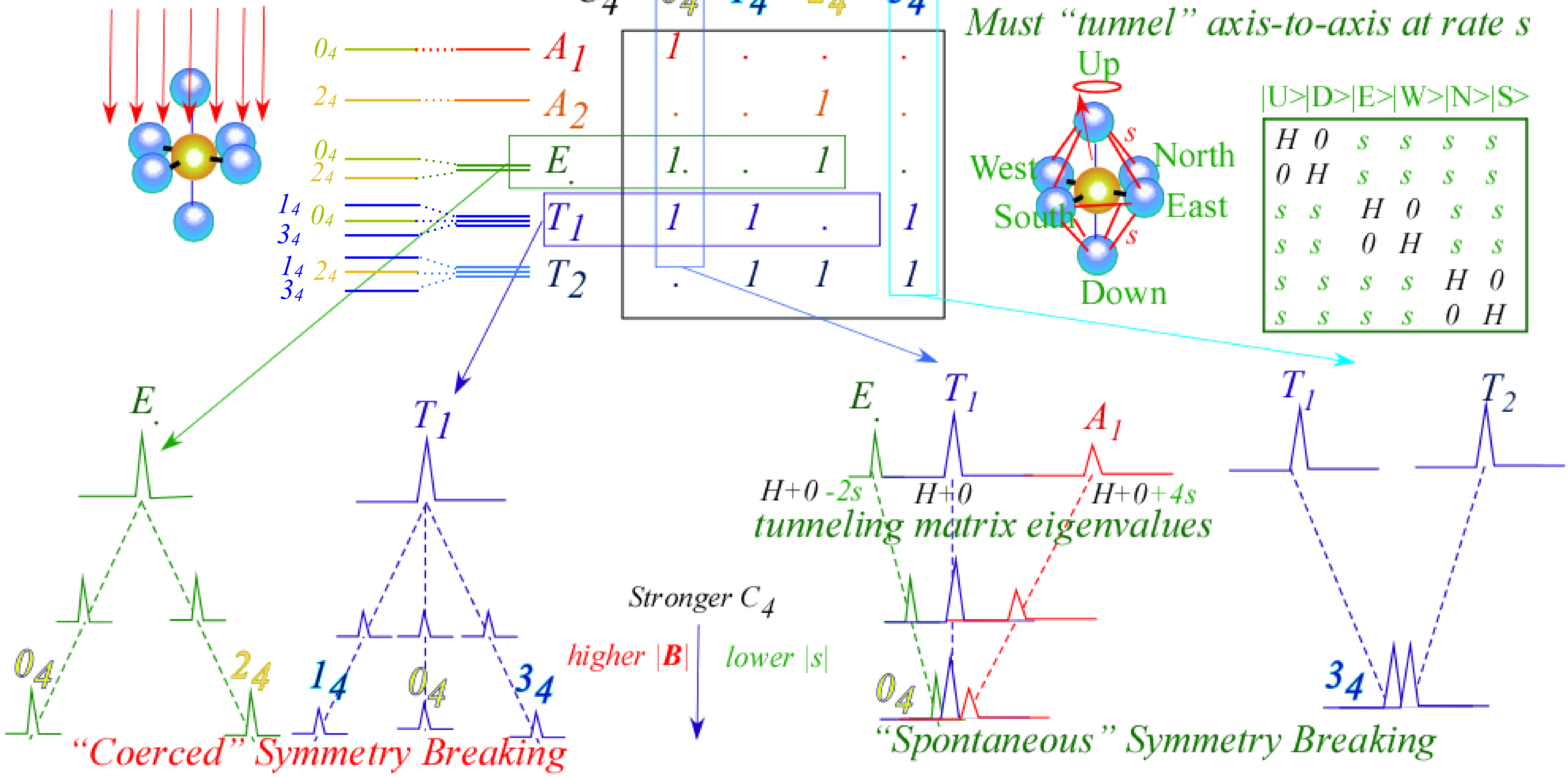
OUTSIDE versus INSIDE

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



$$\begin{array}{c|cccc} C_4 & 0_4 & 1_4 & 2_4 & 3_4 \\ \hline A_1 & 1 & . & . & . \\ A_2 & . & . & 1 & . \\ E & 1. & . & 1 & . \\ T_1 & 1 & 1 & . & 1 \\ T_2 & . & 1 & 1 & 1 \end{array}$$

$$\begin{array}{cccccc} |U\rangle & |D\rangle & |E\rangle & |W\rangle & |N\rangle & |S\rangle \\ H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{array}$$

$H+0$ $-2s$ $H+0$ $H+0+4s$

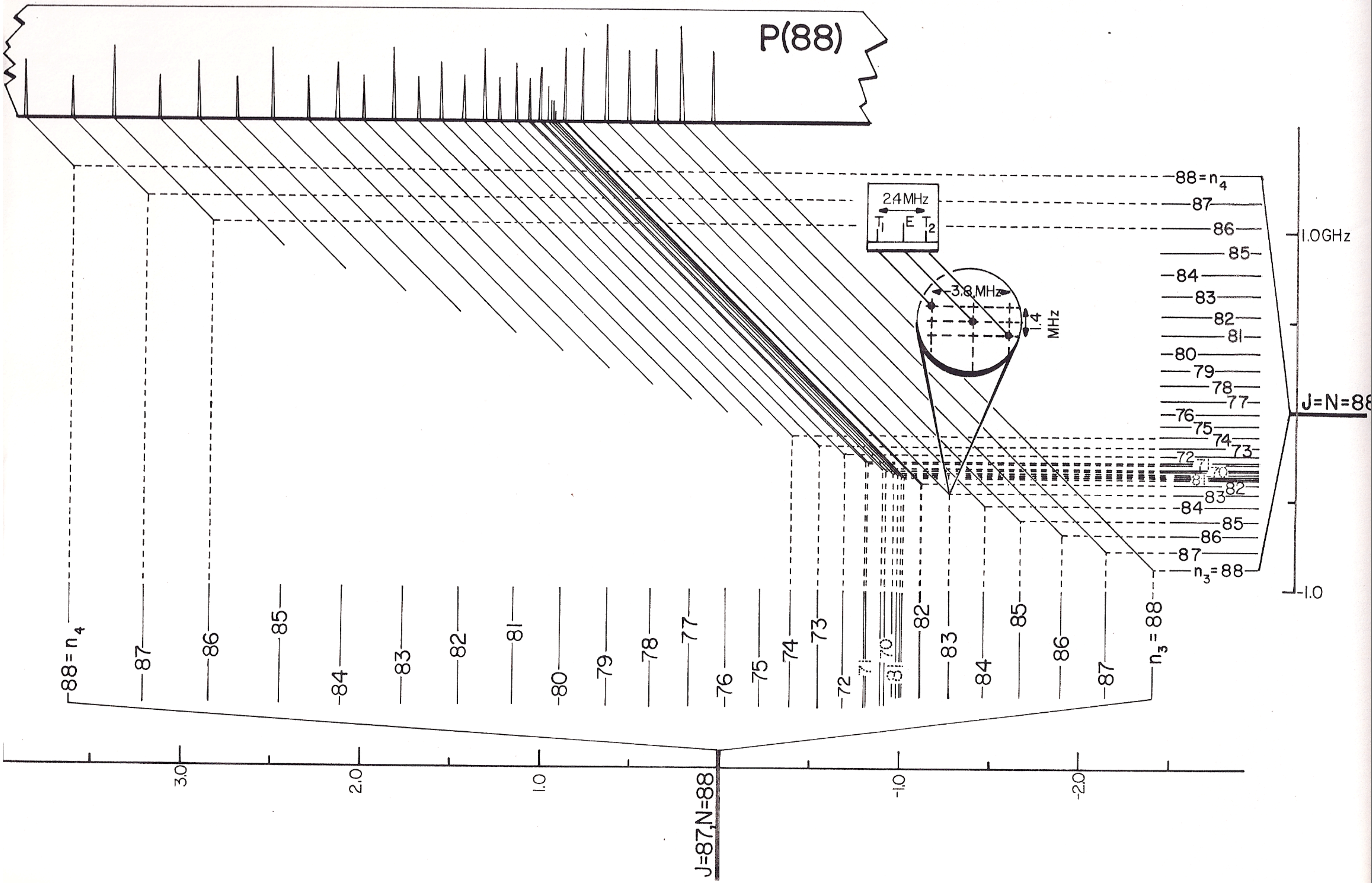
tunneling matrix eigenvalues

Stronger C_4

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

"Coerced" Symmetry Breaking

"Spontaneous" Symmetry Breaking


P(88)
88=n4
87
86
85
84
83
82
81
80
79
78
77
76
75
74
73
72
71
70
81
82
83
84
85
86
87
n3=88
2.4 MHz
T1
E
T2
3.8 MHz
1.4 MHz
1.0GHz
-1.0
J=N=88
J=87, N=88
3.0
2.0
1.0
-1.0
-2.0

Details of $P(88)$ ν_4 SF_6 and $P(88)$ ν_4 CF_4 spectral structure and implications

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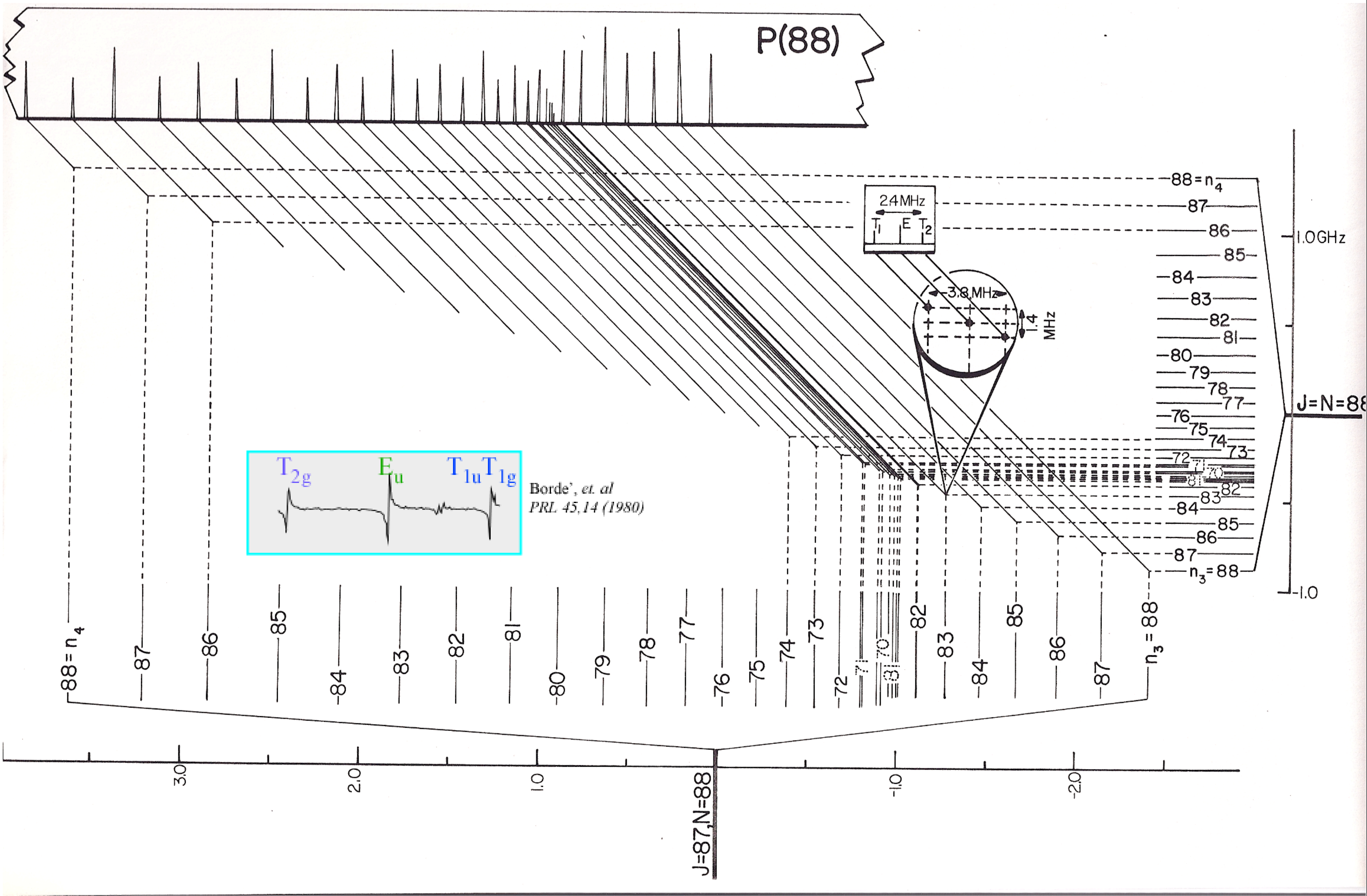
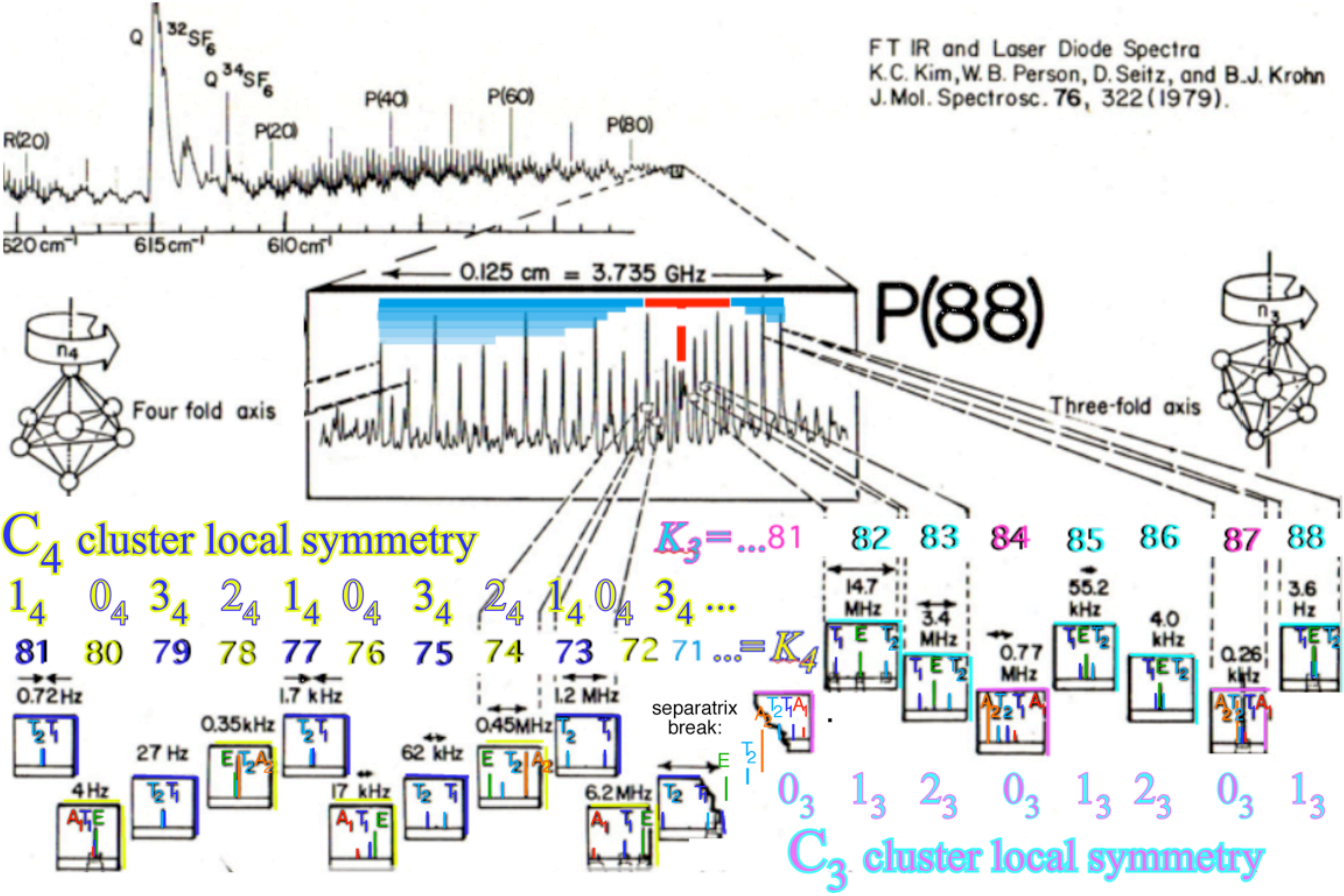
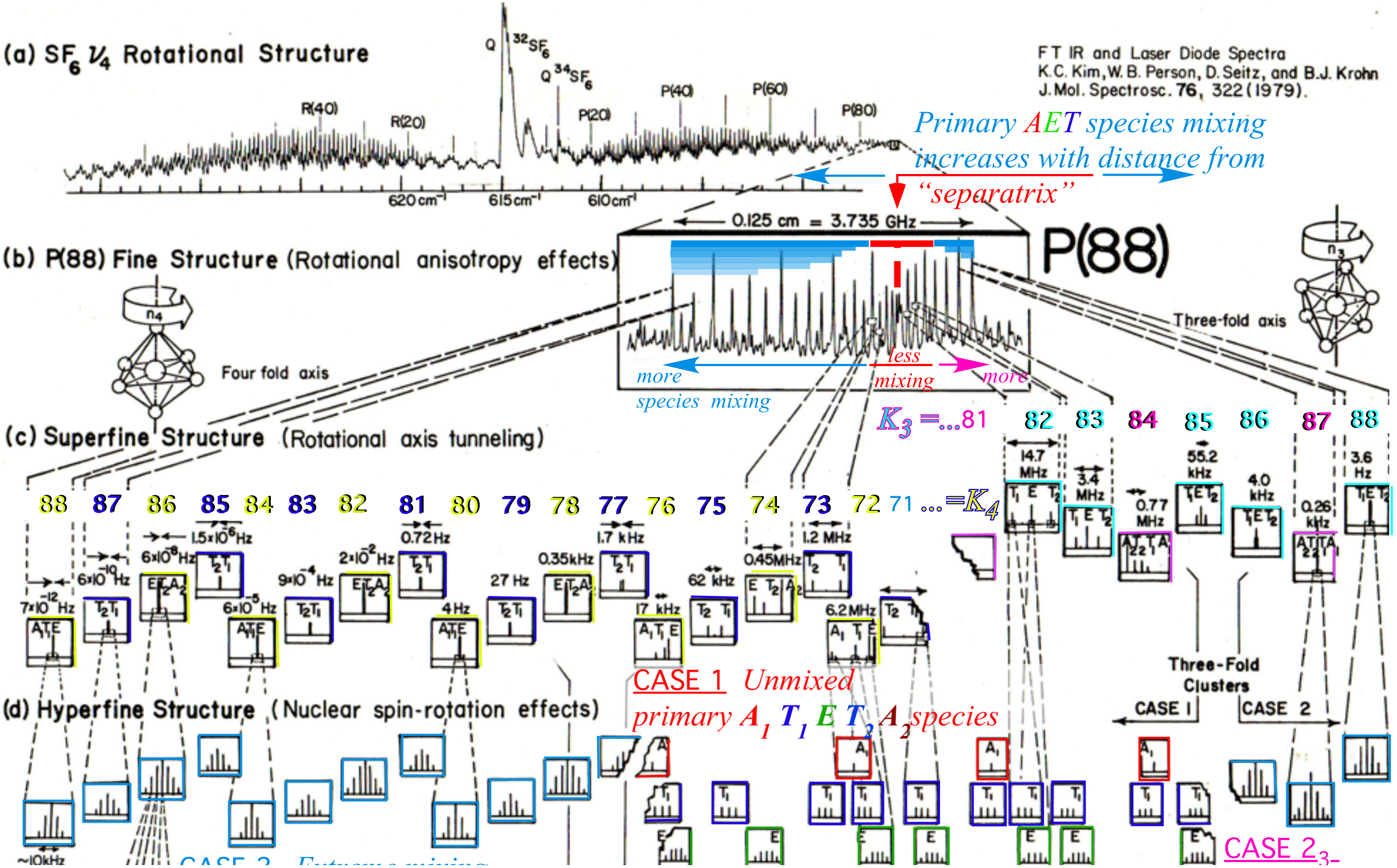


Borde', *et. al*
PRL 45,14 (1980)

IR Spectra of SF6 ν_4 P(88)


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

Int.J.Molecular Science 14.(2013) Fig.26 p. 783



(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).

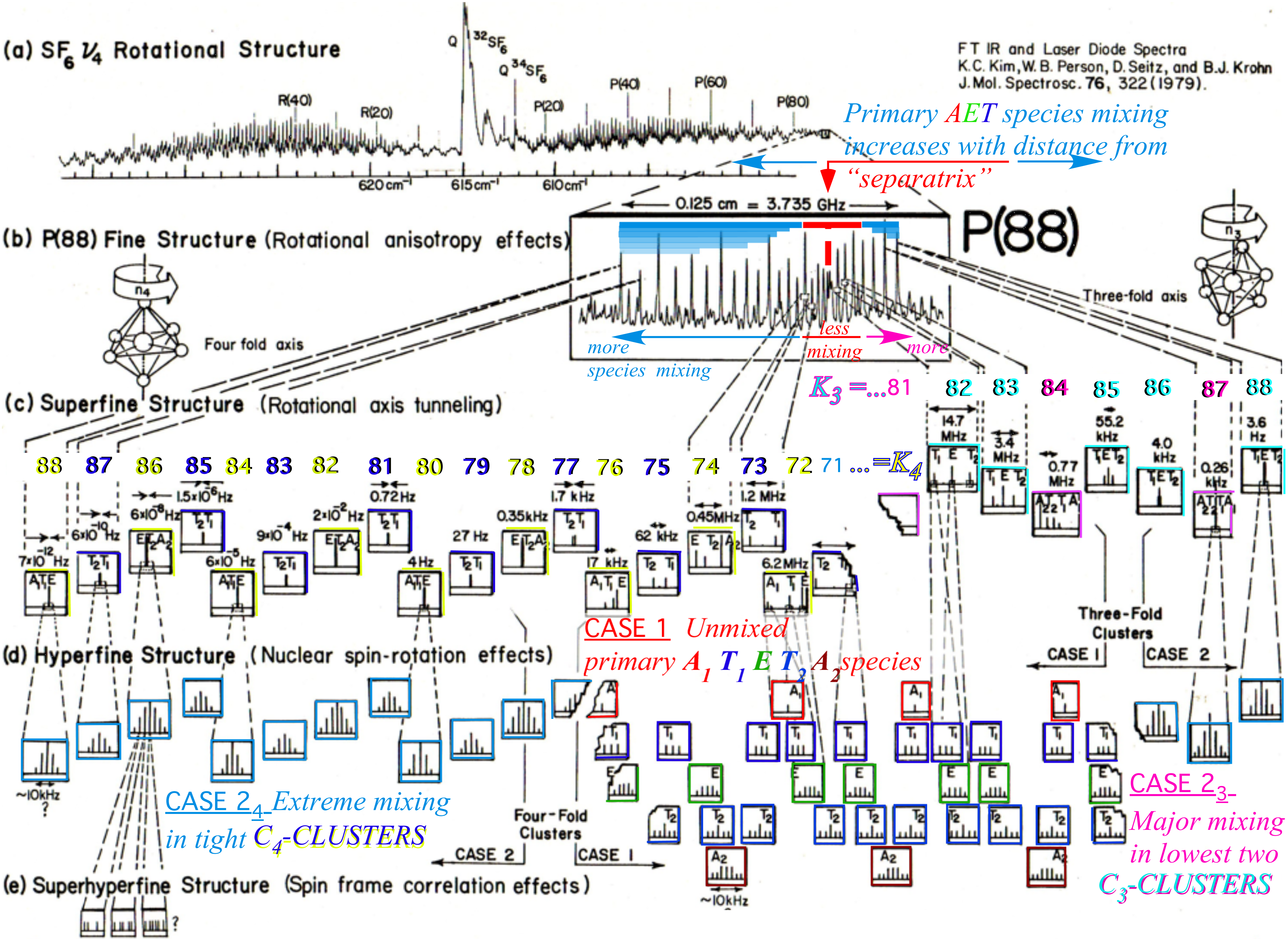
Primary AET species mixing increases with distance from "separatrix"

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

(c) Superfine Structure (Rotational axis tunneling)

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

CASE 1 *Unmixed primary A_1 T_1 E T_2 A_2 species*



Primary AET species mixing increases with distance from “separatrix”

more species mixing

less mixing

more

K_3 =...81 82 83 84 85 86 87 88

88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...$=K_4$

CASE 1 *Unmixed primary A_1 T_1 E T_2 A_2 species*

CASE 2_4 *Extreme mixing in tight C_4-CLUSTERS*

CASE 2_3 *Major mixing in lowest two C_3-CLUSTERS*

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Graphical approach to rotation-vibration-spin Hamiltonian

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

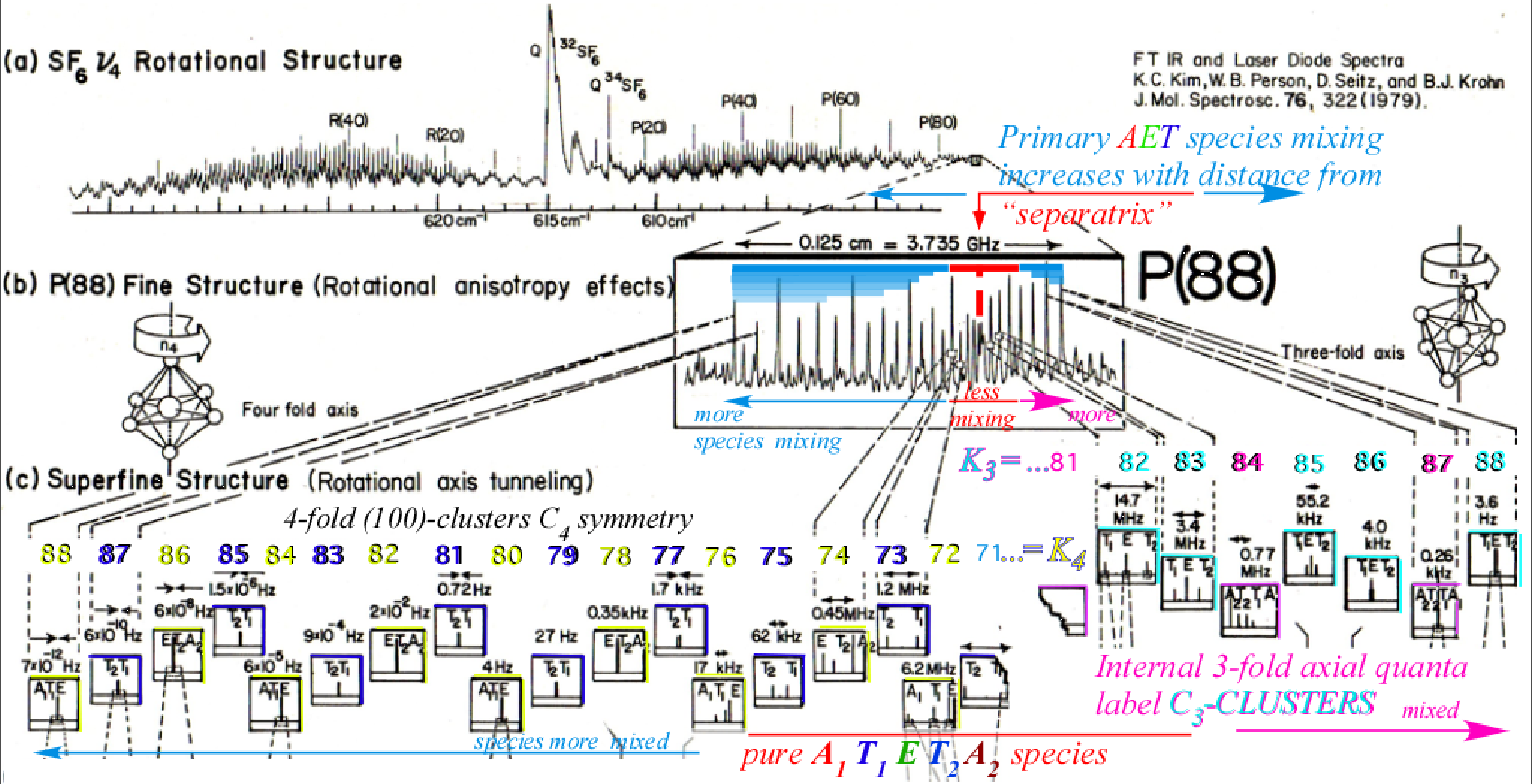
OUTLINE

Introductory review — Example(s)

- *Rovibronic nomograms and PQR structure* — ν_3 and ν_4 SF_6
- *Rotational Energy Surfaces (RES) and θ^J_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



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Primary AET species mixing increases with distance from "separatrix"

more species mixing

less mixing

more

$K_3 = \ldots 81$ 82 83 84 85 86 87 88

4-fold (100)-clusters C_4 symmetry

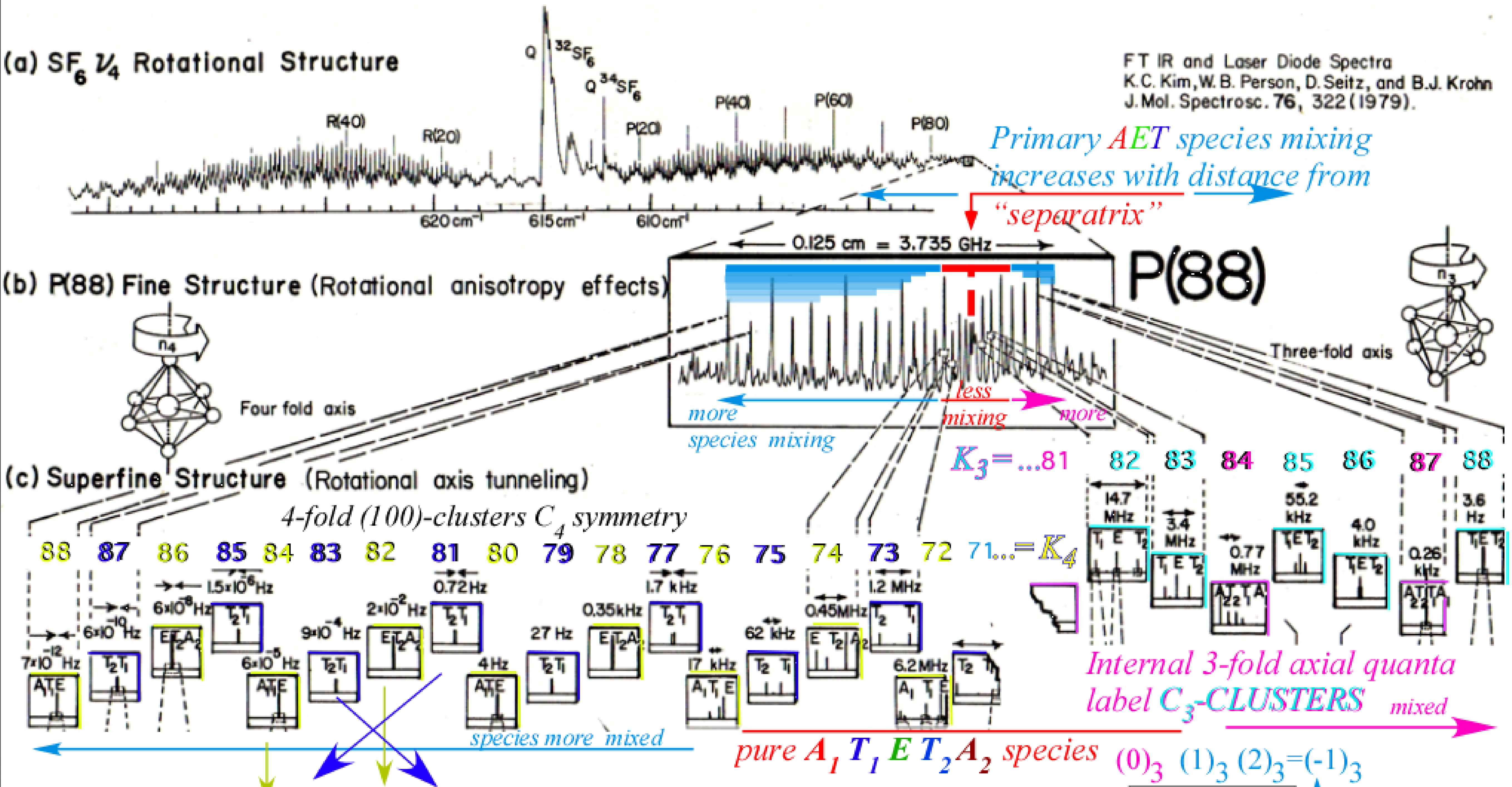
$71\ldots = K_4$

Internal 3-fold axial quanta label C_3-CLUSTERS

mixed

species more mixed

pure A_1 T_1 E T_2 A_2 species



Primary *AET* species mixing increases with distance from "separatrix"

more species mixing

less mixing

more

K_3= ...81

4-fold (100)-clusters C_4 symmetry

71...= K_4

Internal 3-fold axial quanta label C_3-CLUSTERS

mixed

species more mixed

pure A_1 T_1 E T_2 A_2 species

Cubic Octahedral symmetry *O*

	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

3 modulo 4 equals -1 modulo 4 (and 83 mod 4)

83=84-1

4-fold (1oo) C_4 symmetry clusters

3-fold (111) C_3 symmetry clusters

	$(0)_3$	$(1)_3$	$(2)_3=(-1)_3$
A_1	1	•	•
A_2	1	•	•
E	•	1	1
T_1	1	1	1
T_2	1	1	1

(2 modulo 3 equals -1 modulo 3 and 86 mod 3)

86=88-1

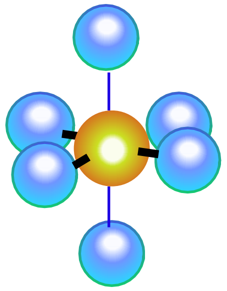
Entanglement!

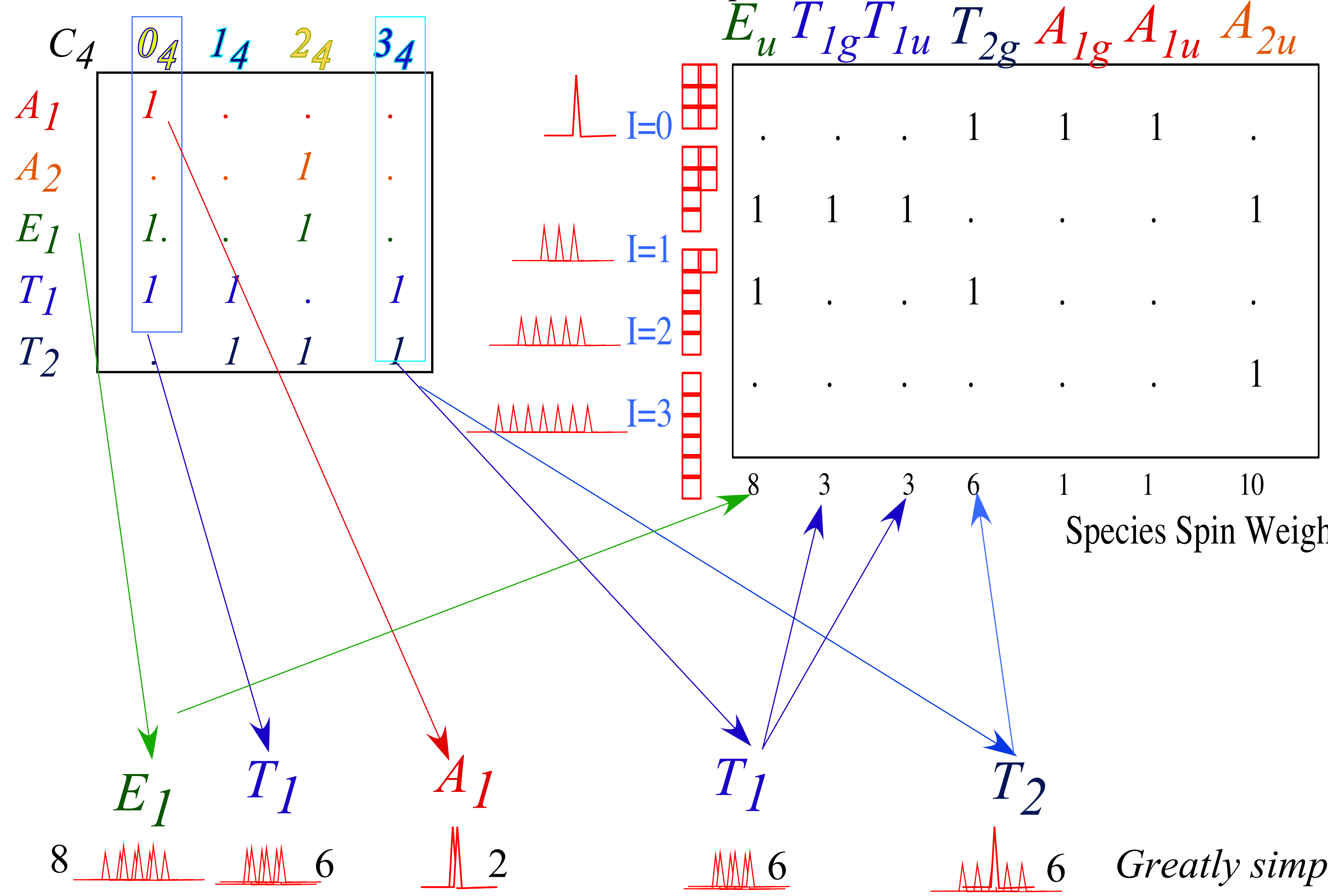
How F-nuclei become entangled

total-spin-I-symmetry O_h species

in SF_6.

With rotation all six ● nuclei are equivalent





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-Permutation to Octahedral Correlations $S_6 \supset O_h$

	E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
I=0	.	.	.	1	1	1	.
I=1	1	1	1	.	.	.	1
I=2	1	.	.	1	.	.	.
I=3	.	.	.	.	.	.	1
Species Spin Weights	8	3	3	6	1	1	10

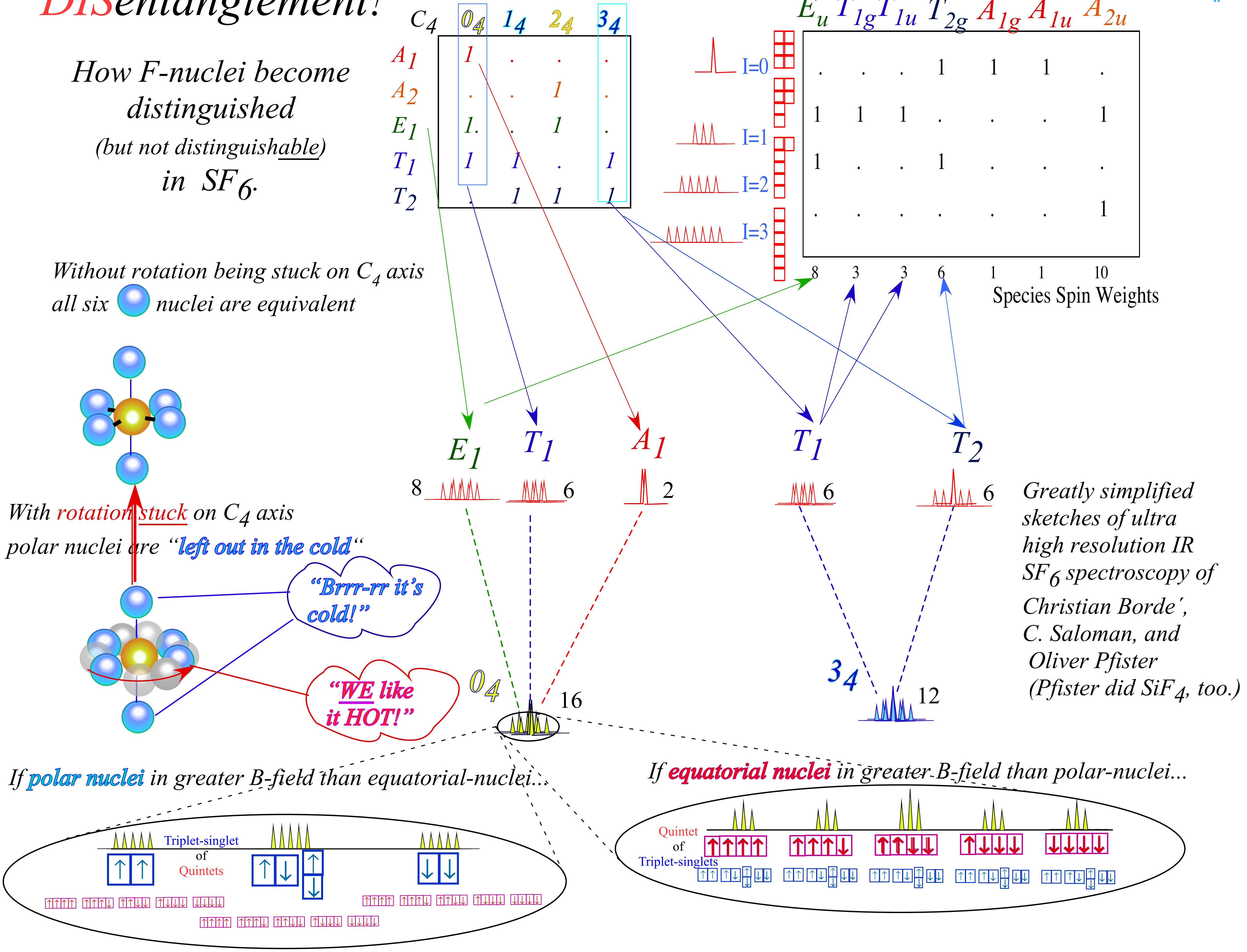
Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister (Pfister did SiF_4, too.)

DISentanglement!

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



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

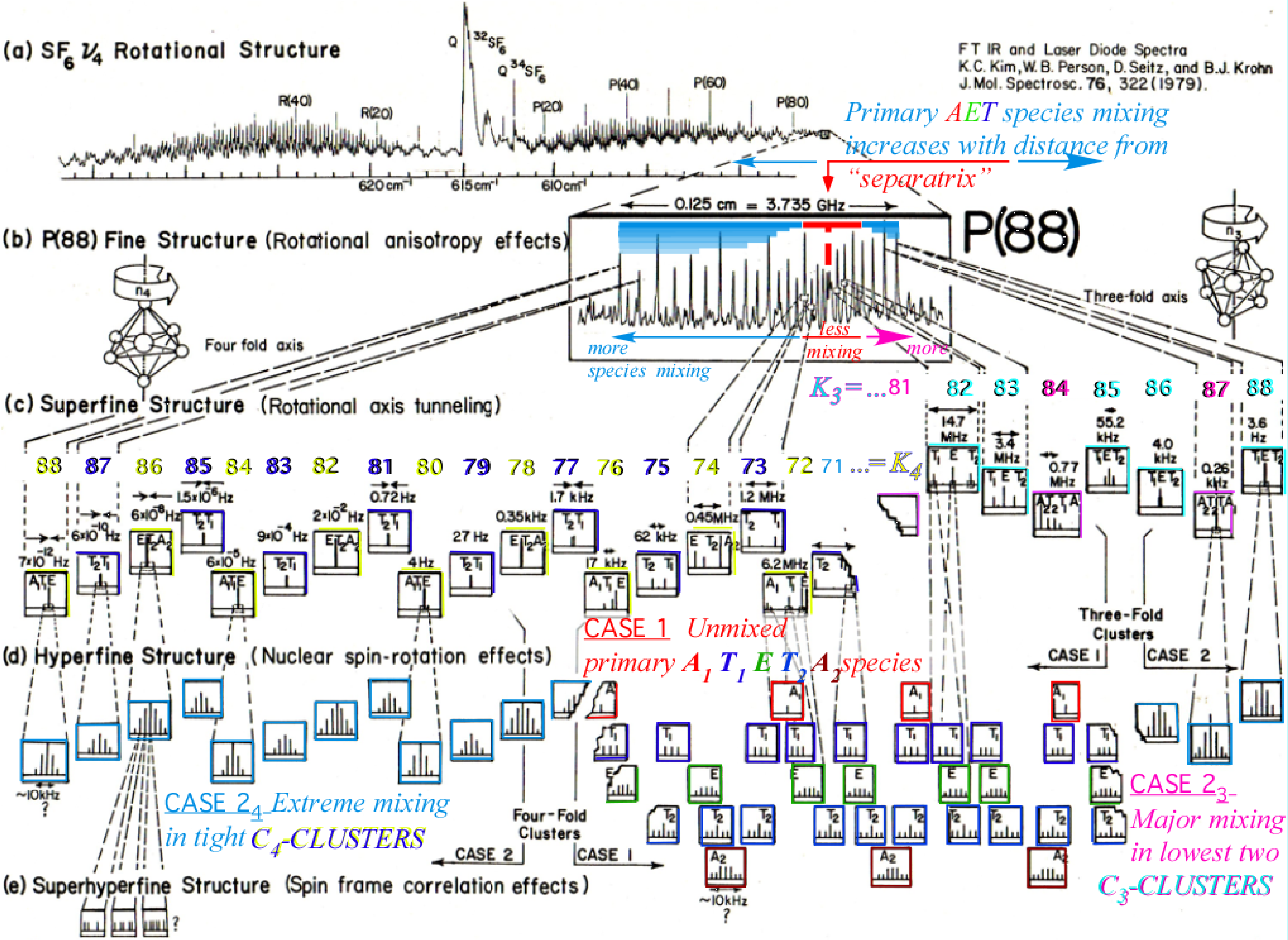
Spin-Permutation to Octahedral Correlations $S_6 \supset O_h$

	E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
I=0	.	.	.	1	1	1	.
I=1	1	1	1	.	.	.	1
I=2	1	.	.	1	.	.	.
I=3	.	.	.	.	.	.	1
Species Spin Weights	8	3	3	6	1	1	10

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...*



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more species mixing

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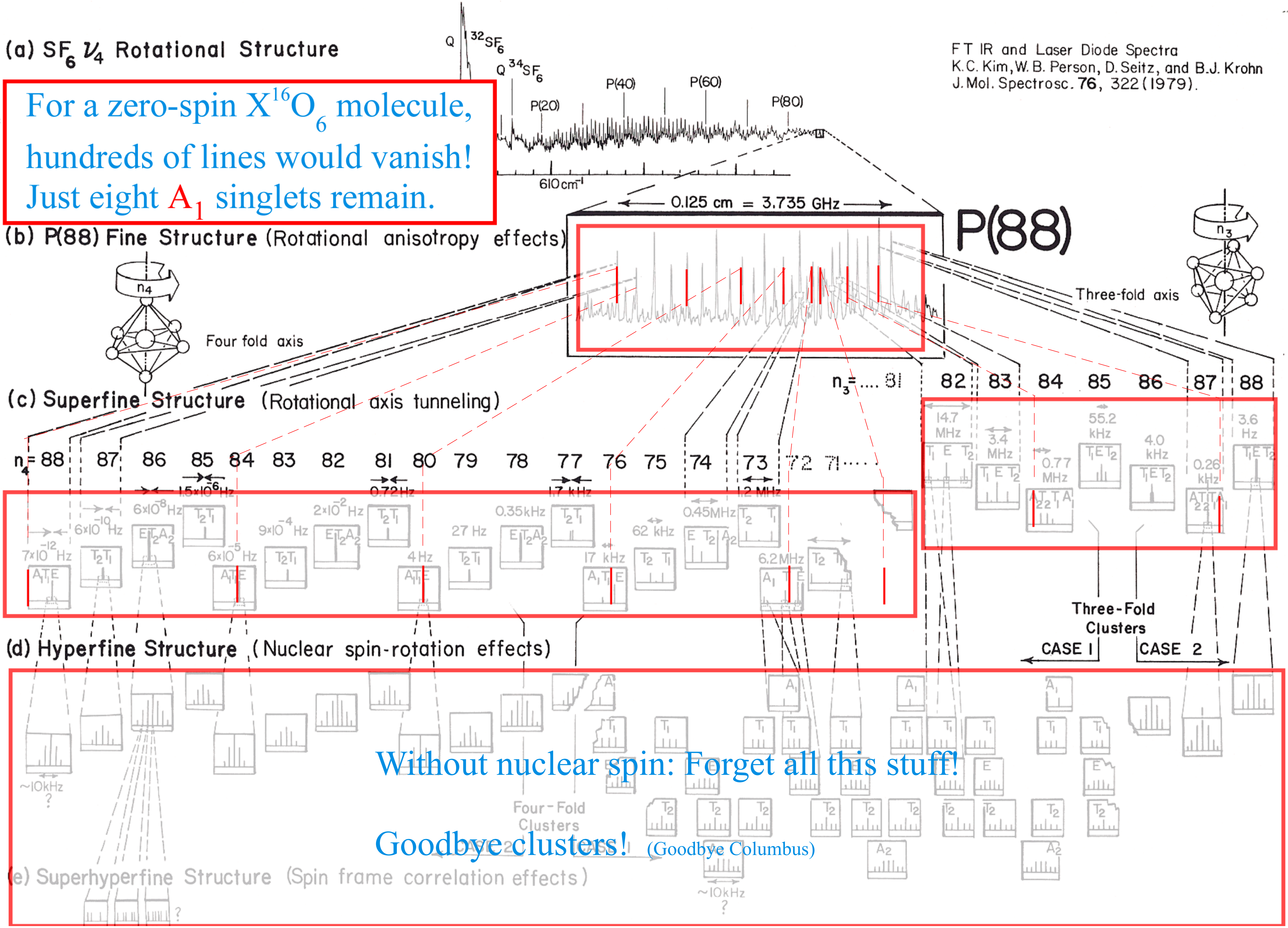


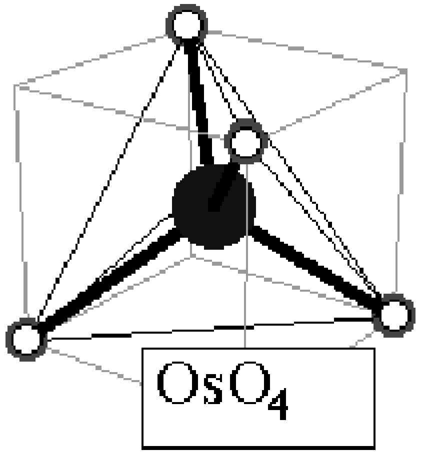
For a zero-spin X^{16}O$_6$ molecule, hundreds of lines would vanish! Just eight A_1 singlets remain.

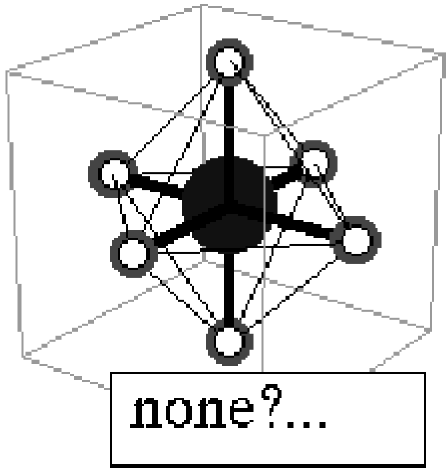
Without nuclear spin: Forget all this stuff!

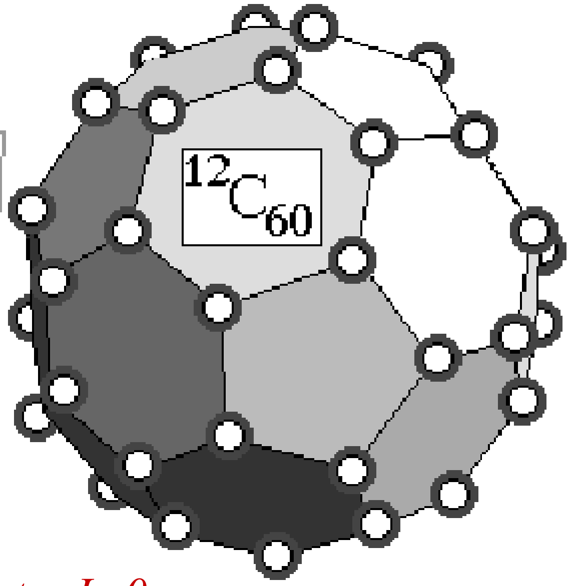
Goodbye clusters! (Goodbye Columbus)

Some examples of Bose Exclusion

Spherical Top Molecules with Spin-0 Nuclei

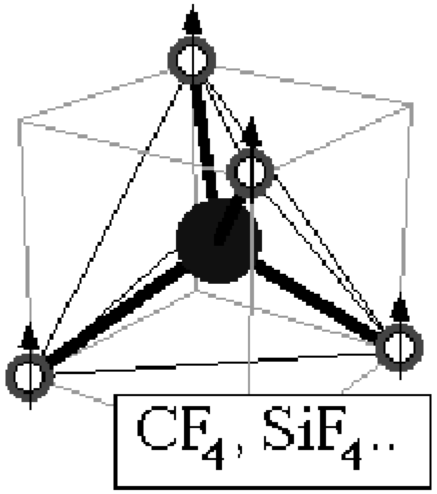




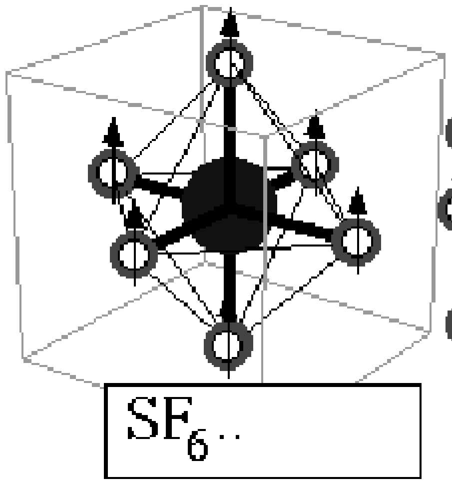


Only 1 hyperfine state: I=0

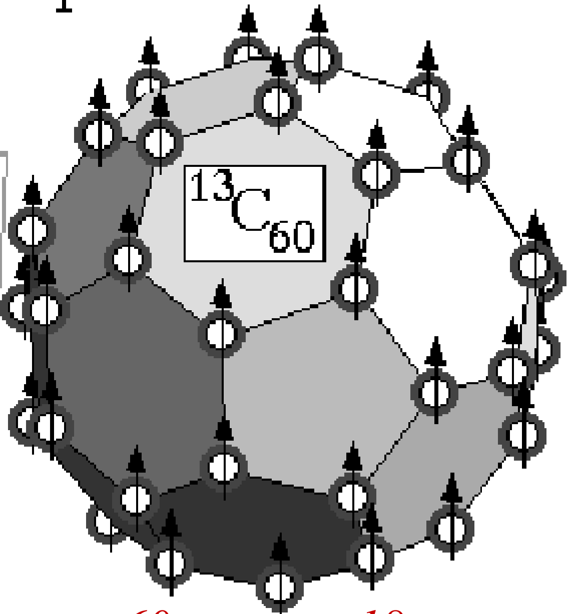
Spherical Top Molecules with Spin-1/2 Nuclei



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



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

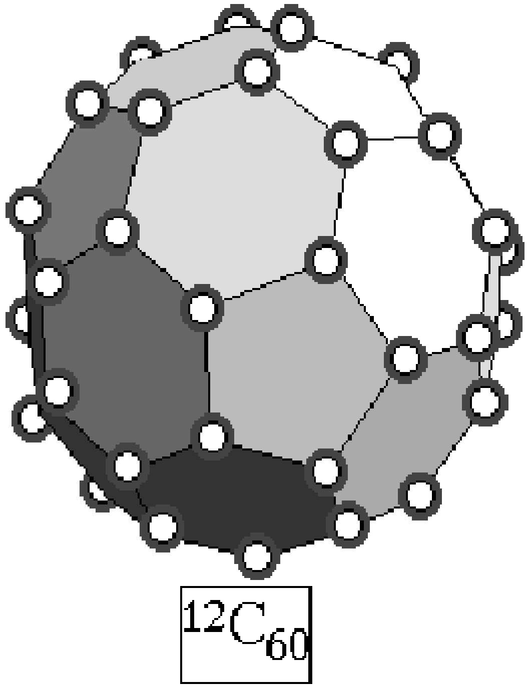


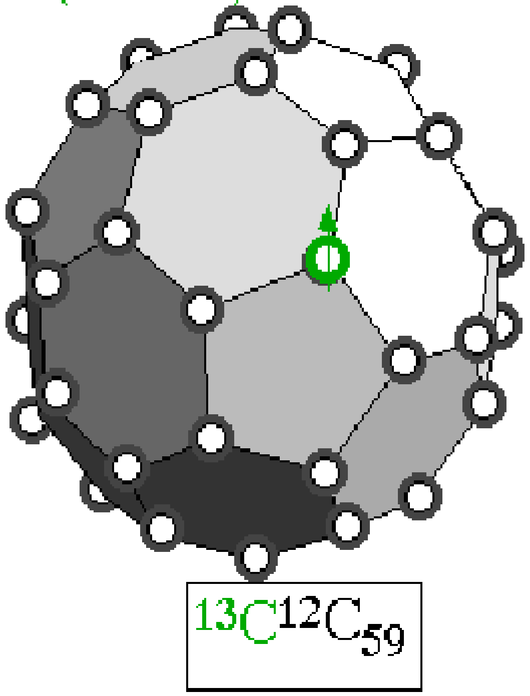
2^{60}=1.15x10^{18} hyperfine states: I=0-30

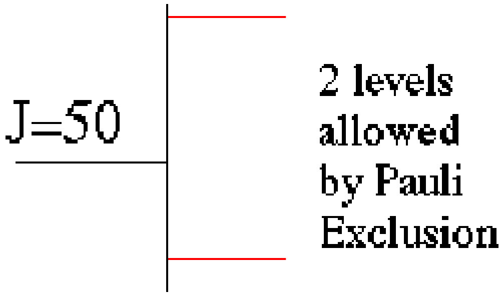
Example of extreme symmetry exclusion

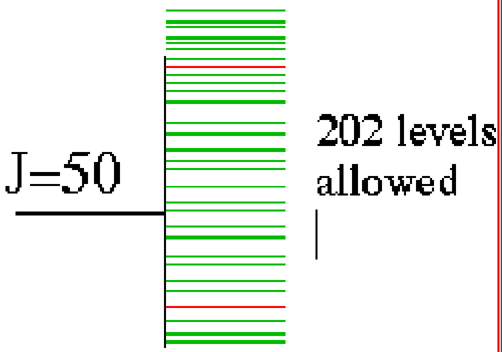
... (and partial recovery)

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

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CONSERVATION OF ROVIBRONIC SPECIES - *Two Views:*

Old
(1939, 1945, and 1966)

"...transitions between...species (A_1,..E,..T_2..)
...are **very strictly forbidden**.. *"*

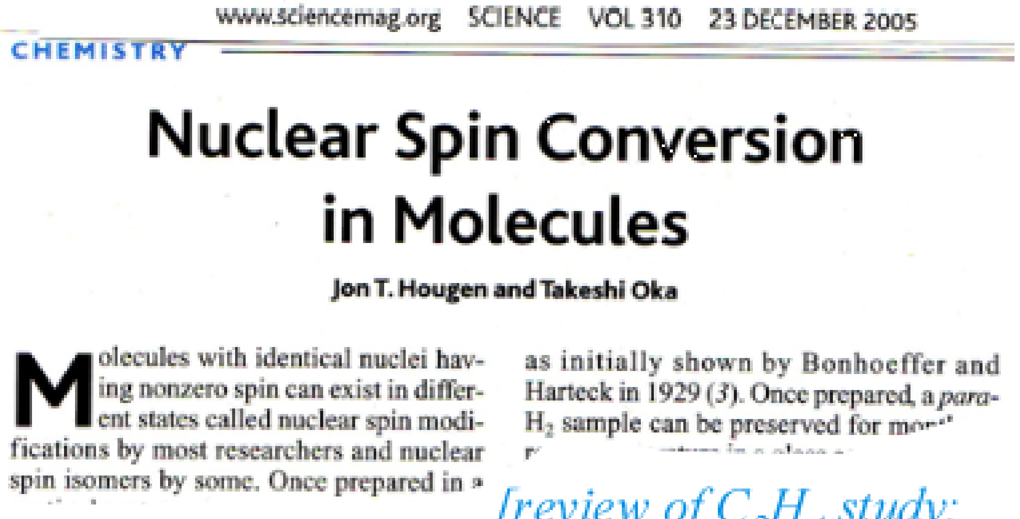
...for diatomic molecules...I p. 150
...for D_2 asymmetric tops...II p.468
...for D_n symmetric tops...II p.415
...for O-T_d spherical tops...II p.441-453

...during transitions involving...

...rotational states,...III p.246
...vibrational states,... " "
... electronic states,... " "
... collisional states... " "

versus

New (1978- present)



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 mo

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

Strictly *versus* ***NOT!***

Conservation and preservation?

To conserve vs. To convert

To preserve vs. To pervert

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

Conversion, perversion or transition?

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)*

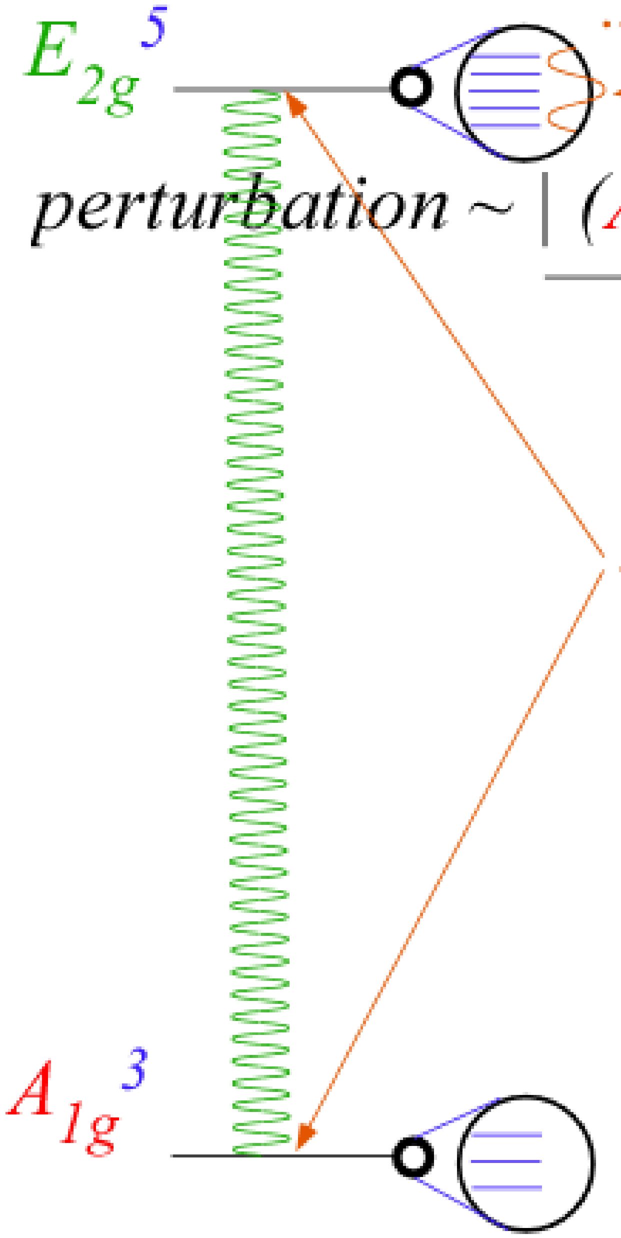
HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

What preserves it? versus What messes it up?

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

No Way!

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



...too darn small (~kHz)...

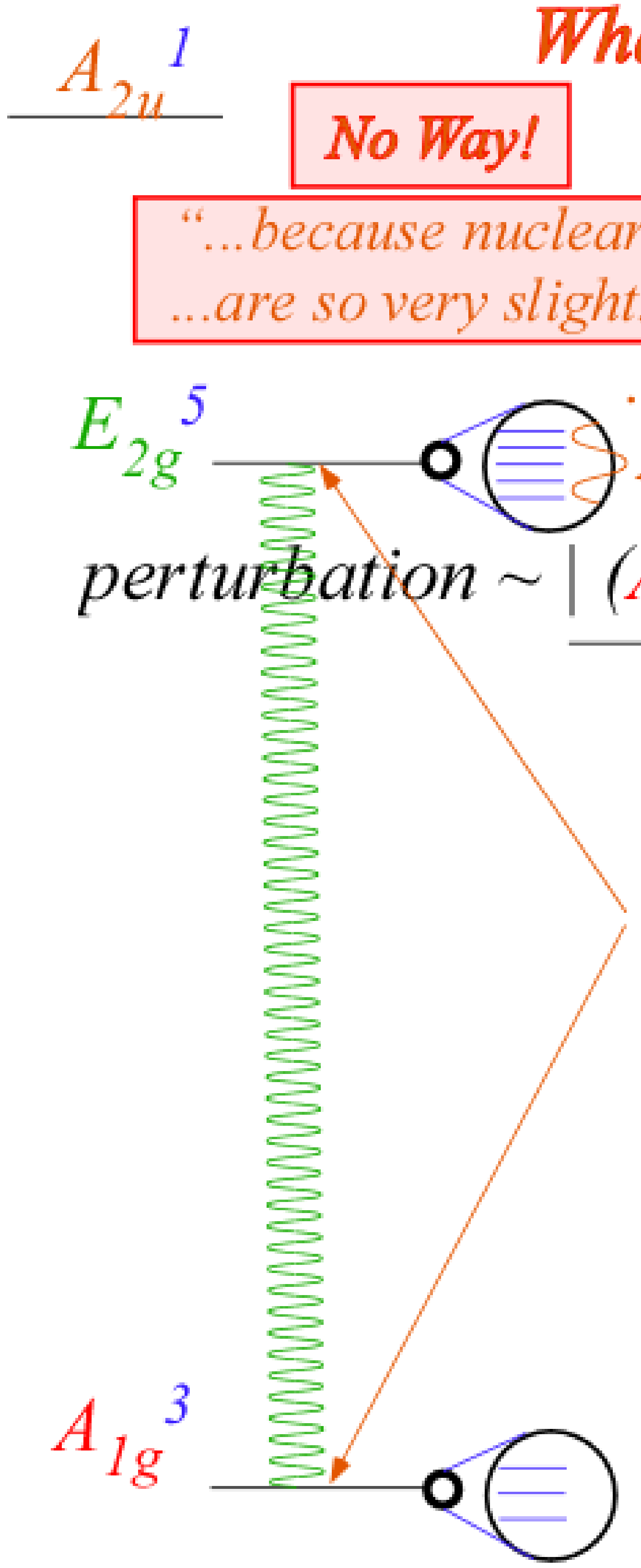
$$\text{perturbation} \sim \frac{\left|\left(A_{1g}{}^{3}\middle|\text{spin-rovib.}\middle|E_{2g}{}^{5}\right)\right|^{2}}{E_{A_{1g}{}^{3}} - E_{E_{2g}{}^{5}}}$$

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

or perverted?

HOW CONSERVED ^ IS ROVIBRONIC-SPIN SYMMETRY?

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



No Way!

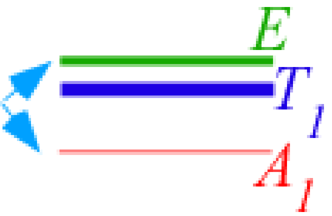
"...because nuclear moments...
...are so very slight..."

...too darn small (~kHz)...

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

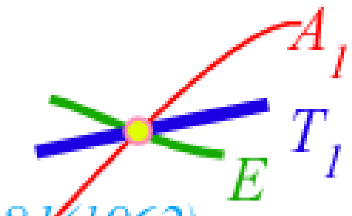
...too darn big (*like* 10MHz)...

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



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! $\mathbf{A_1\ T_1\ E\ T_2\ A_2}$ *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)

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    - *Rotational Energy Eigenvalue Surfaces (REES)*

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

Introductory review

	Example(s)
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and θ^J_K-cones*	ν_4 P(88) SF_6
• *Spin symmetry correlation tunneling and entanglement*	SF_6

Recent developments

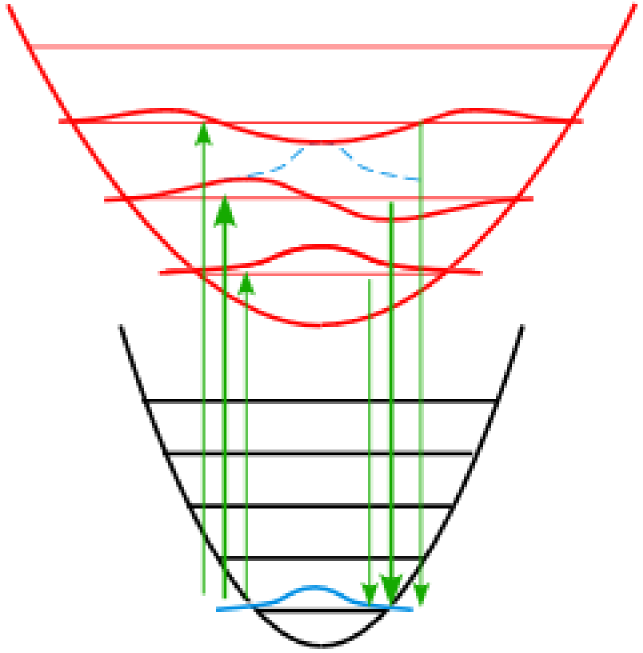
• *Analogy between PE surface and RES dynamics*	
• *Rotational Energy Eigenvalue Surfaces (REES)*	ν_3 SF_6

Potenial Energy Surface (PES) Dynamics

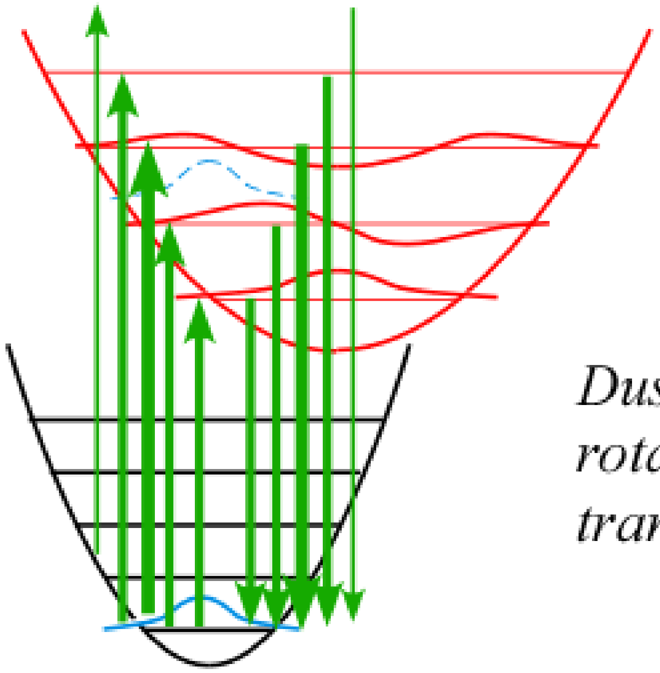
Inter-PES electronic transitions

Vibrational Franck-Condon effects

- Frequency mismatch of PES



- Shape or position mismatch of PES



Duschinsky rotation or translation

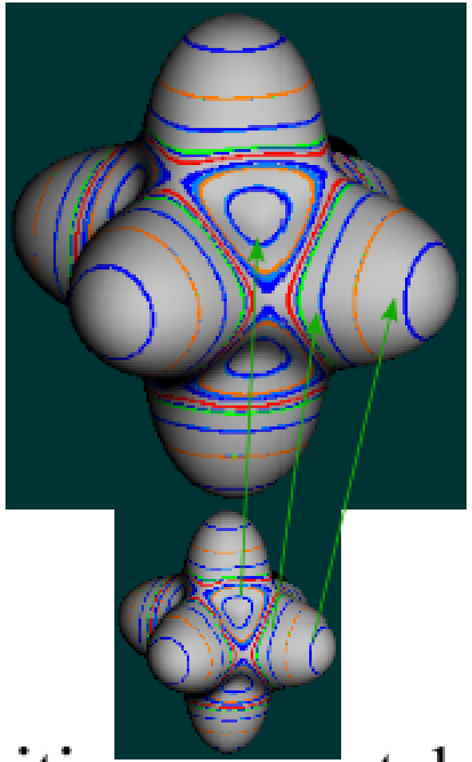
Analogy between Vibronic and Rovibronic

Rotation Energy Surface (RES) Dynamics

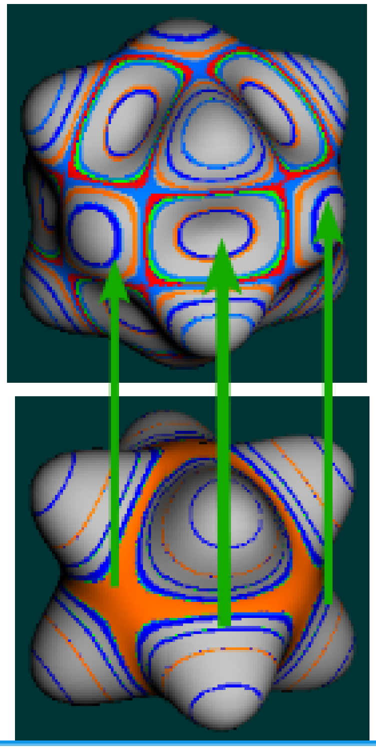
Inter-PES electronic transitions

Rotational "Franck-Condon" effects

- Frequency mismatch of RES



- Shape or position mismatch of RES



Non-Born-Oppenheimer Surfaces

Strong vibration-electronic mixing

Jahn-Teller-Renner effects

- Multiple and variable conformer minima

Rotation Energy Eigen-Surfaces (REES)

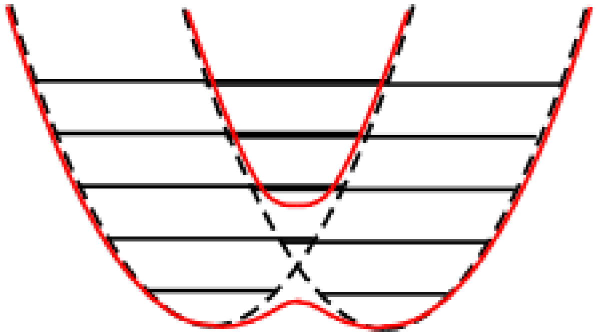
Inter-PES electronic transitions

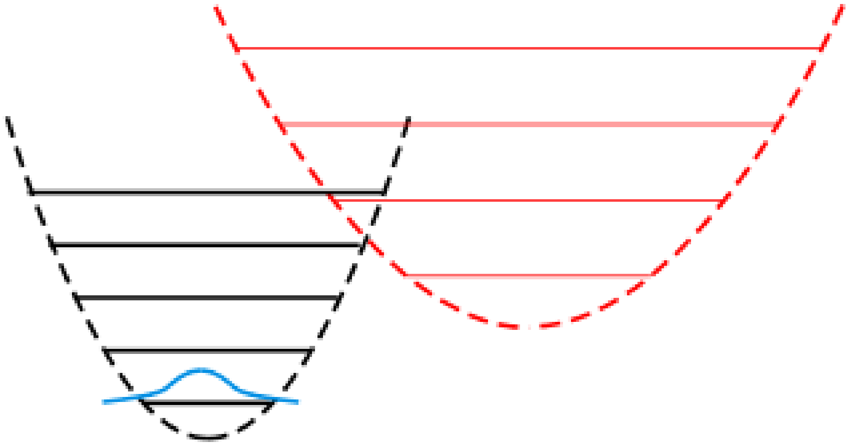
Rotational JTR effects

- Multiple and variable J-axes

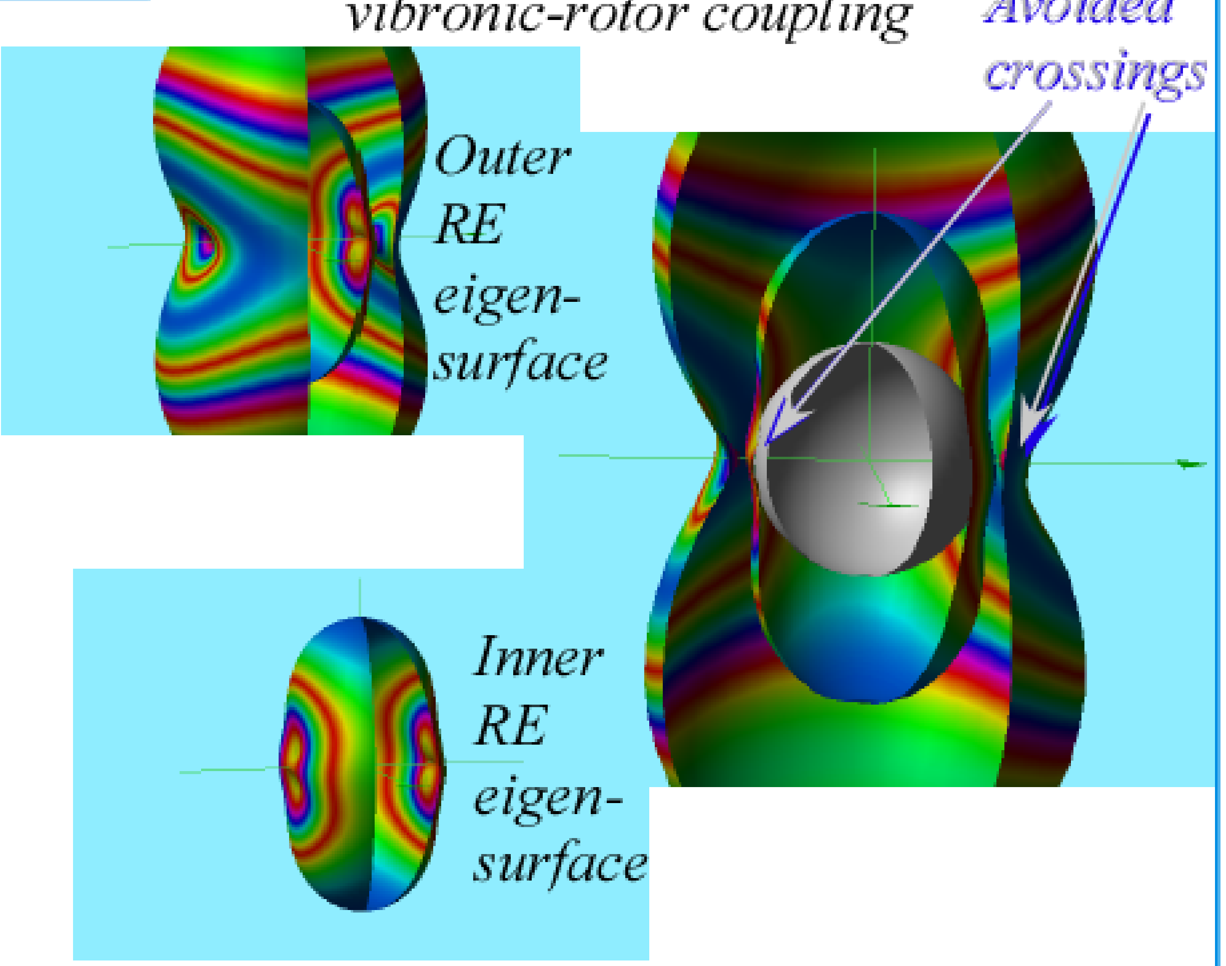
Analogy between

Vibronic and Rovibronic



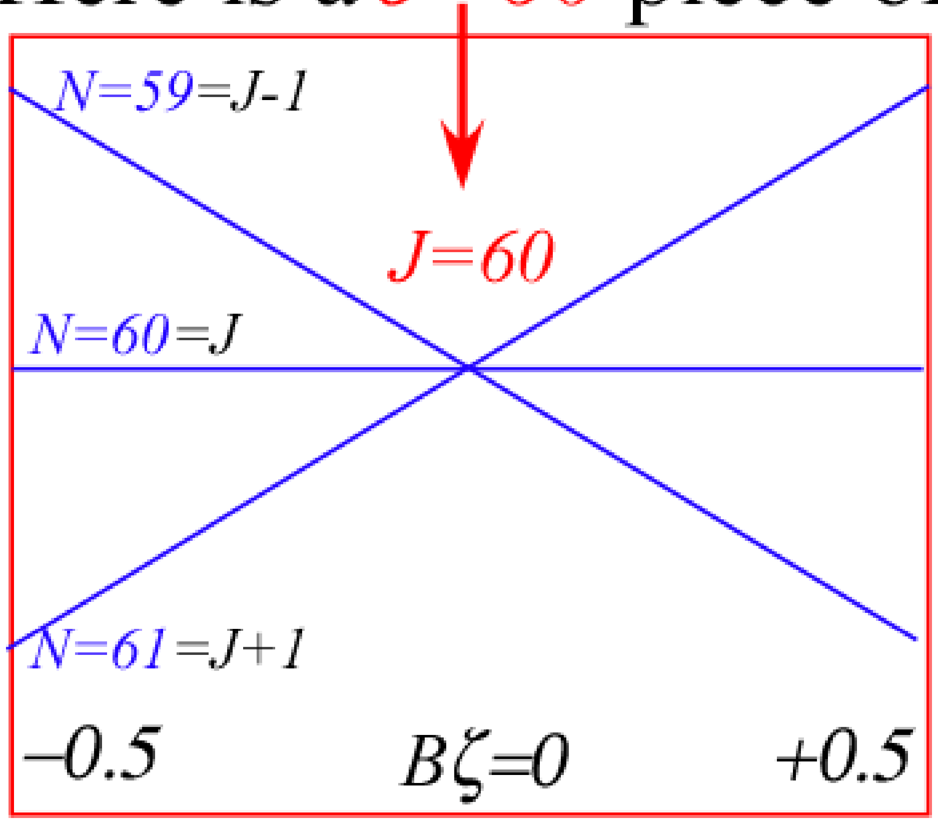


Example for 2-state vibronic-rotor coupling



Recall scalar Coriolis *PQR* plots vs. $B\zeta$

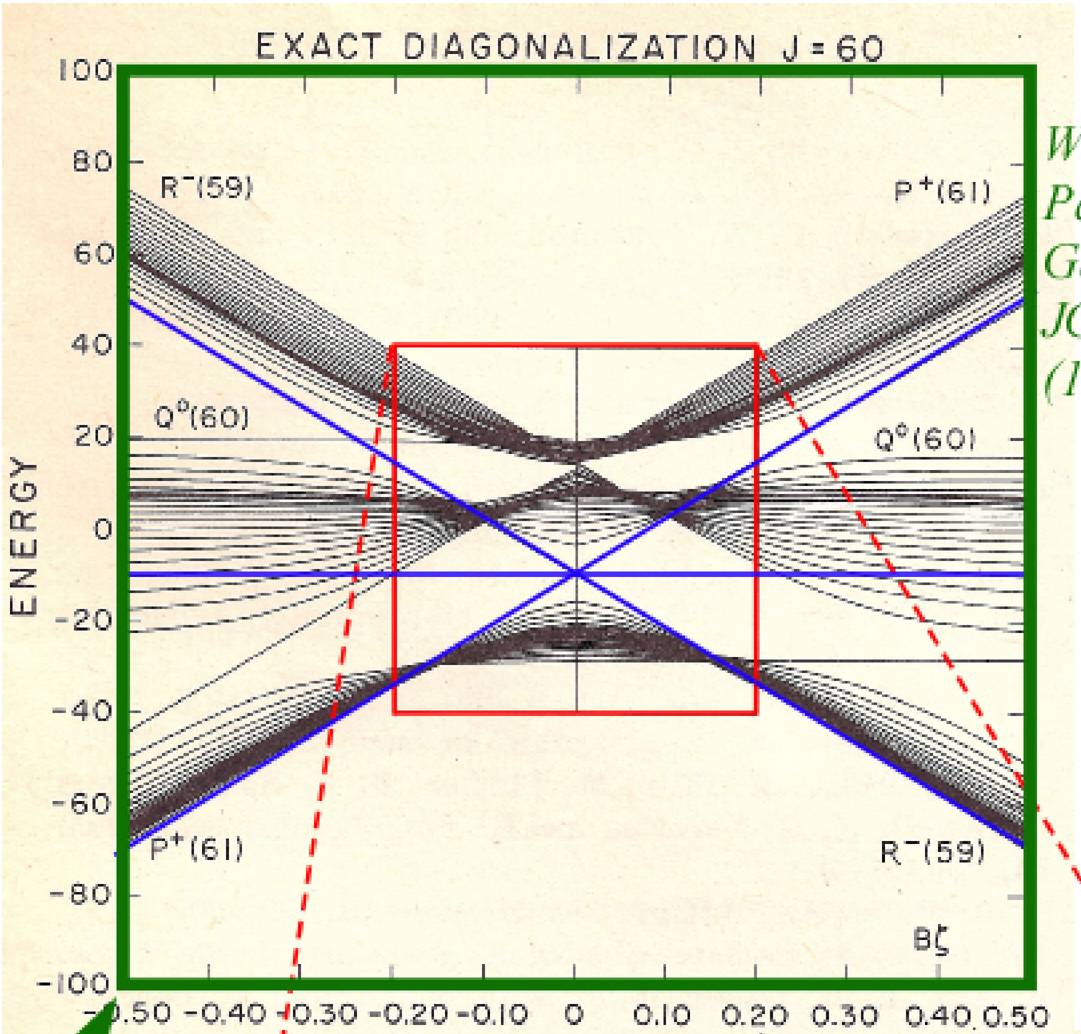
Here is a *J=60* piece of it:



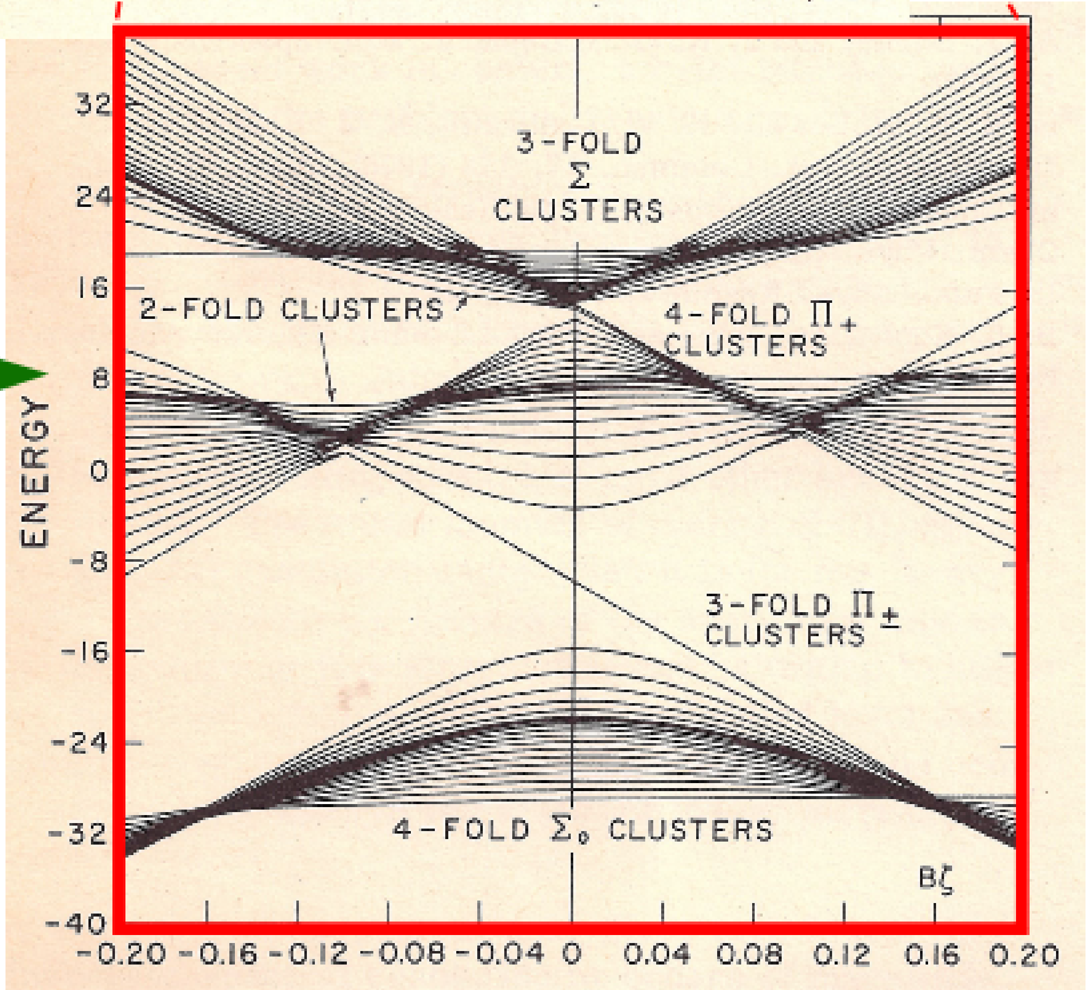
Now consider this plot with *tensor* Coriolis, too

(Just 4th-rank $[2x2]^4$ tensor here.

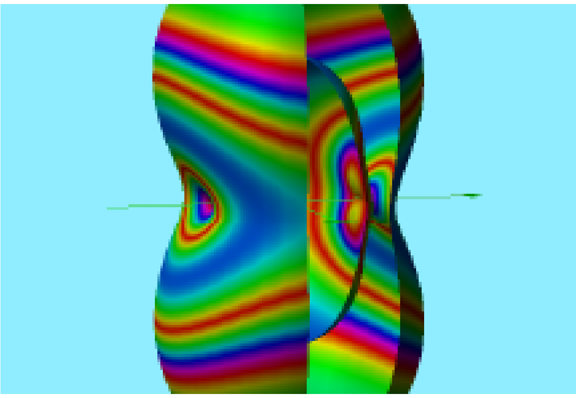
See next talk **RJ06** and a 4PM talk **RI09** by ***Mitchell** et. al.* and ***Boudon** et. al.* who will pull much higher rank!)



WGH, Patterson, Galbraith JCP 69, 4906 (1978)



How to display such monstrous avoided cluster crossings: REES: *Rotational Energy Eigenvalue Surfaces*



Vibration (or vibronic) momentum ℓ retains its quantum representaion(s).

For $\ell=1$ that is the usual *3-by-3* matrices.

Rotational momentum J is treated semi-classically. $|J|=\sqrt{J(J+1)}$

Usually **J** is written in Euler coordinates: $J_x=|J|\cos\gamma\sin\beta$, etc.

Plot resulting H-matrix eigenvalues *vs.* classical variables.

($\ell=1$) *3-by-3* H-matrix e-values are polar plotted *vs.* azimuth γ and polar β.

Body-ΣΠ±-Basis

$$\langle H\rangle=(\nu_3+B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+2B\zeta|J|\begin{array}{c}\begin{array}{ccc}|\Pi+\rangle & |\Sigma+\rangle & |\Pi-\rangle\end{array}\\ \hline \begin{pmatrix}\cos\beta & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta & 0\\ \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & 0 & \frac{1}{\sqrt{2}}e^{-i\gamma}\sin\beta\\ 0 & \frac{1}{\sqrt{2}}e^{i\gamma}\sin\beta & -\cos\beta\end{pmatrix}\end{array}$$

$$+2t_{224}|J|^2\begin{pmatrix}3\cos^2\beta-1 & -\sqrt{8}e^{-i\gamma}\sin\beta\cos\beta & \sin^2\beta\,(6\cos2\gamma+i4\sin2\gamma)\\ -\sqrt{8}e^{i\gamma}\sin\beta\cos\beta\quad 0 & -6\cos^2\beta+2 & \sqrt{8}e^{-i\gamma}\sin\beta\cos\beta\\ \sin^2\beta\,(6\cos2\gamma-i4\sin2\gamma) & \sqrt{8}e^{i\gamma}\sin\beta\cos\beta & 3\cos^2\beta-1\end{pmatrix}$$

Lab-PQR-Basis

$$\langle H\rangle=(\nu_3+B|J|^2)\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}+2B\zeta|J|\begin{array}{c}|P\rangle|Q\rangle|R\rangle\\ \hline \begin{pmatrix}+1&0&0\\0&0&0\\0&0&-1\end{pmatrix}\end{array}$$

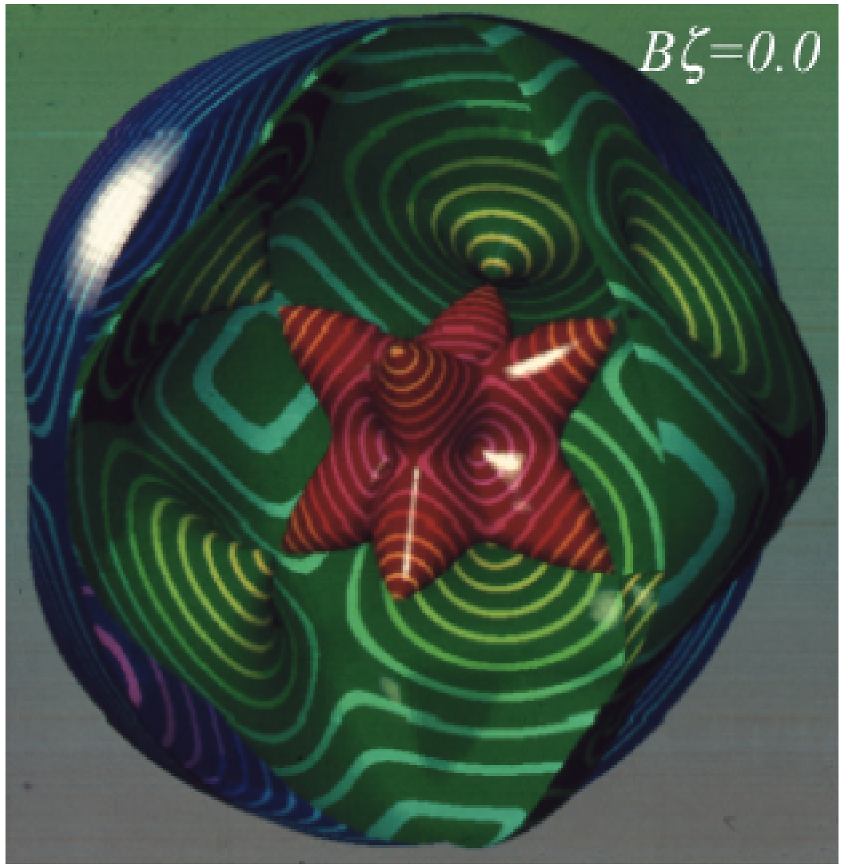
$$+2t_{224}|J|^2\begin{pmatrix}H_{PP}&H_{PQ}&H_{PR}\\H^*_{PQ}&H_{QQ}&H_{QR}\\H^*_{RP}&H^*_{QR}&H_{RR}\end{pmatrix}$$

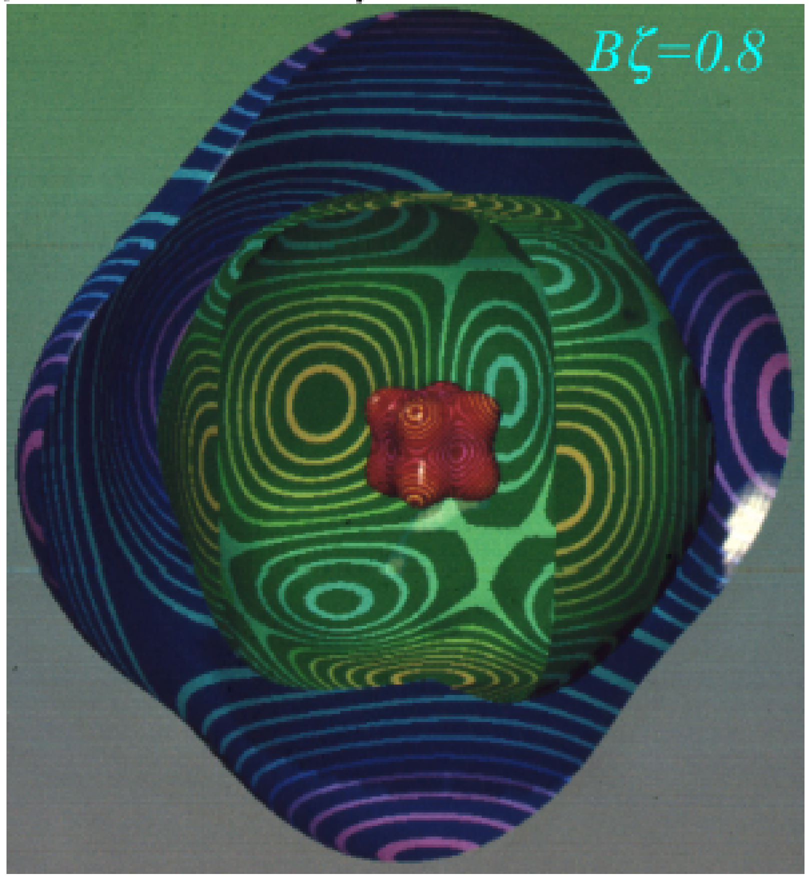
(Either basis should give same REES)

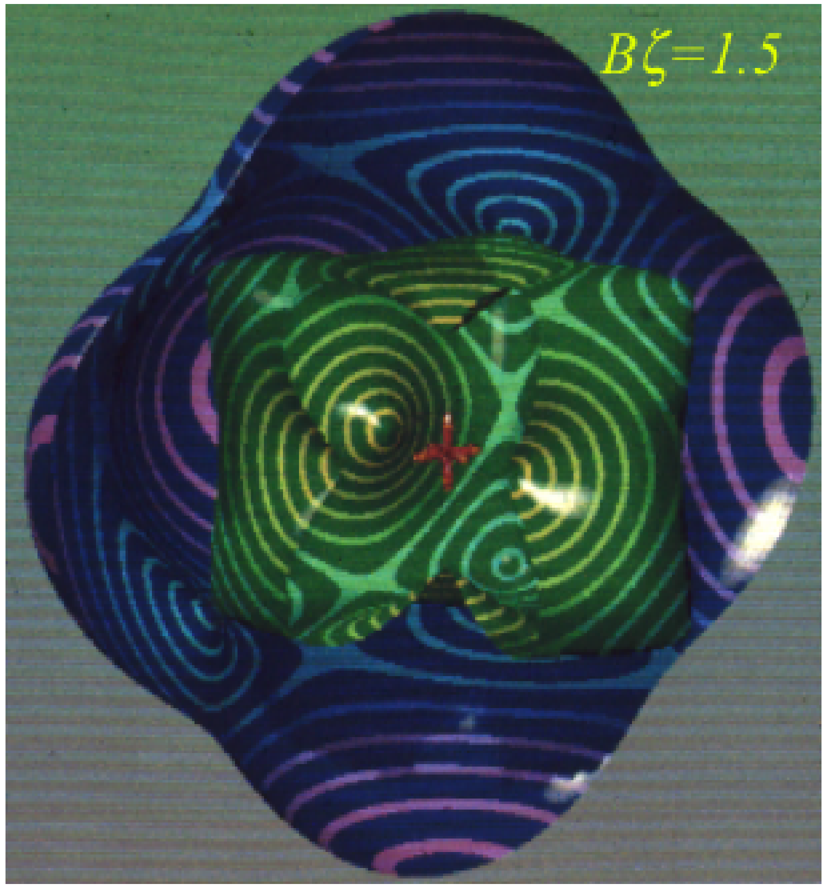
$$H_{PP}=(35\cos^4\beta-30\cos^2\beta+5\sin^2\beta\sin4\gamma+5)/4=H_{RR}$$

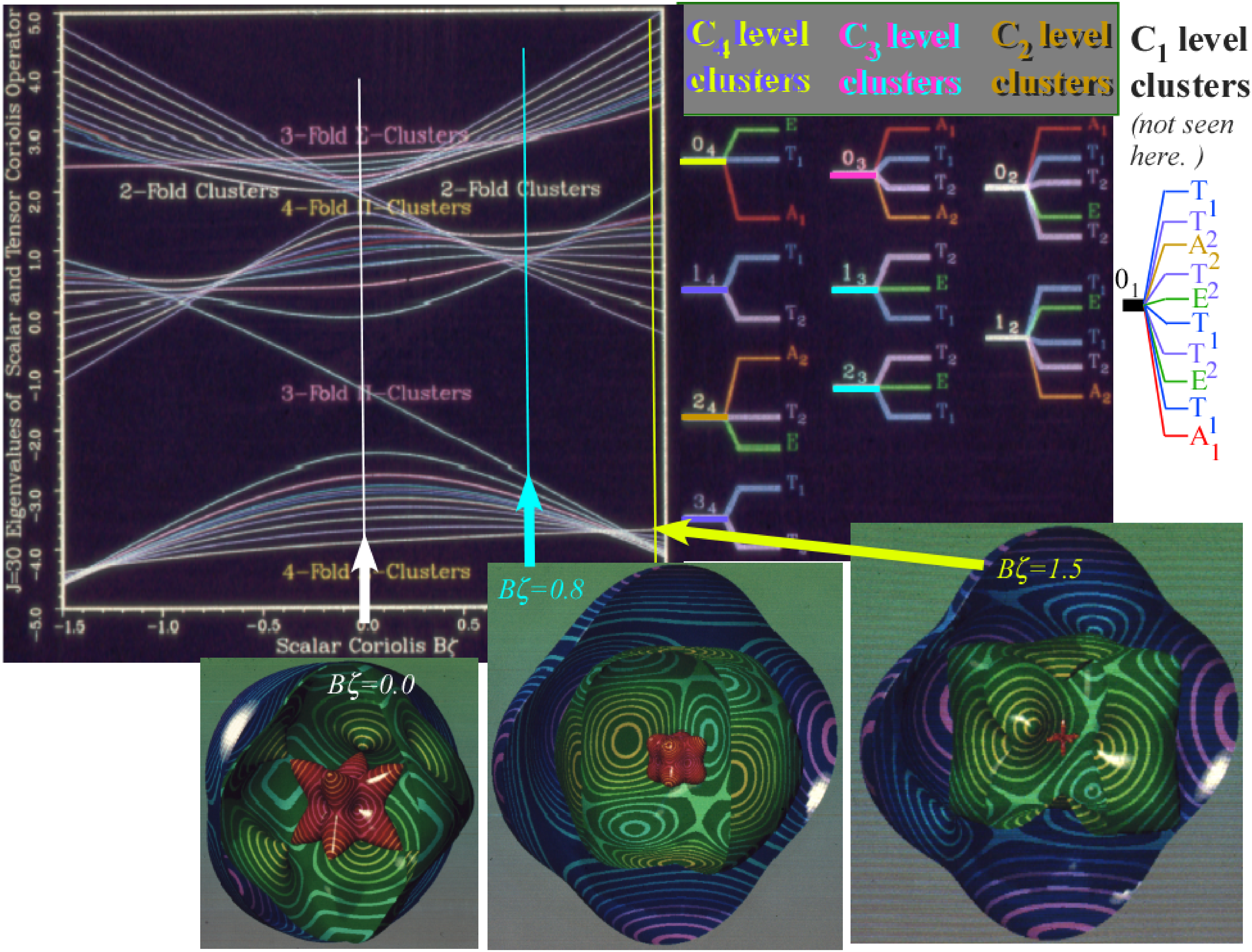
$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

$$H_{PQ}=5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos4\gamma+2i\cos\beta\sin^2\beta\sin4\gamma-1)/4$$





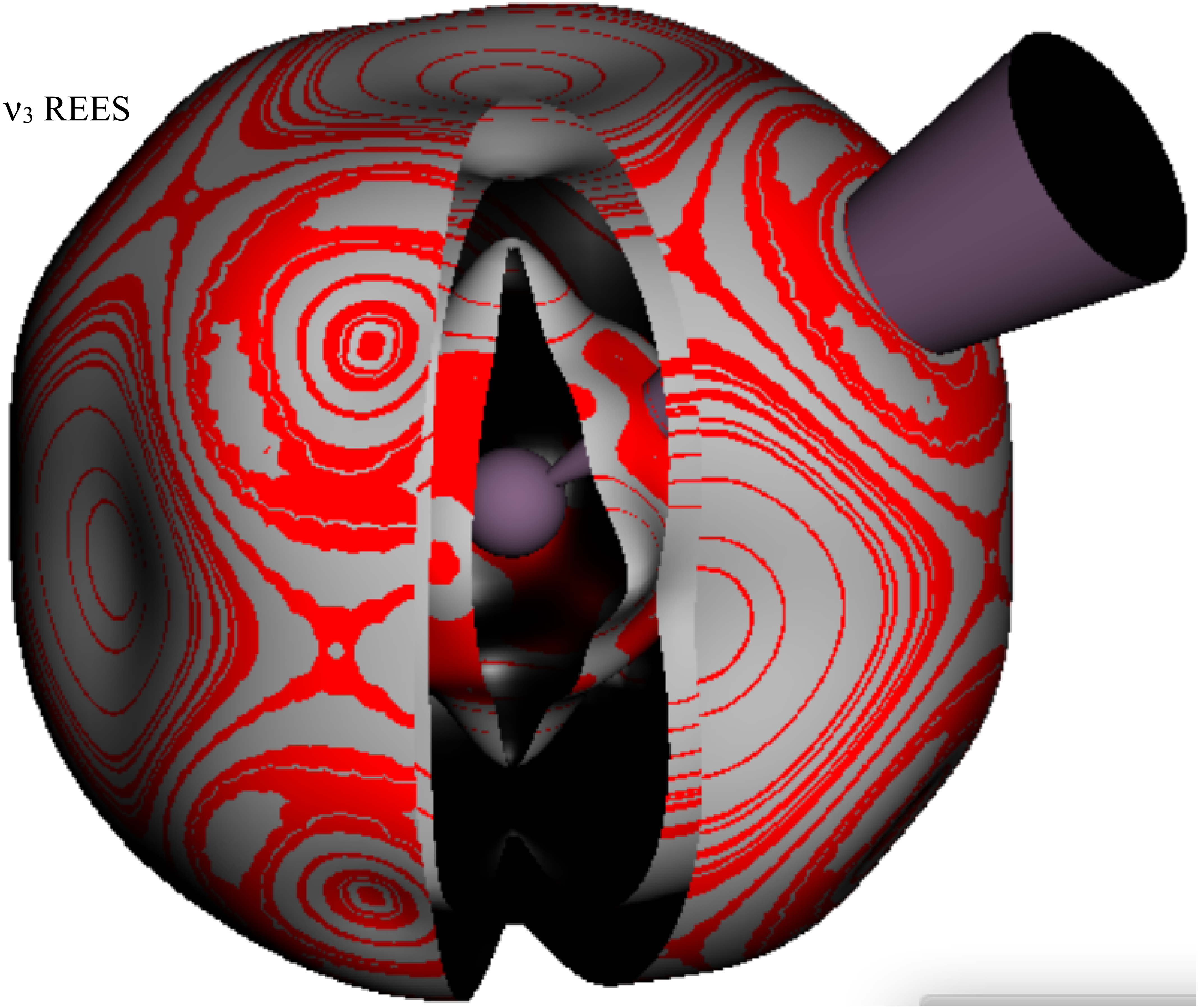


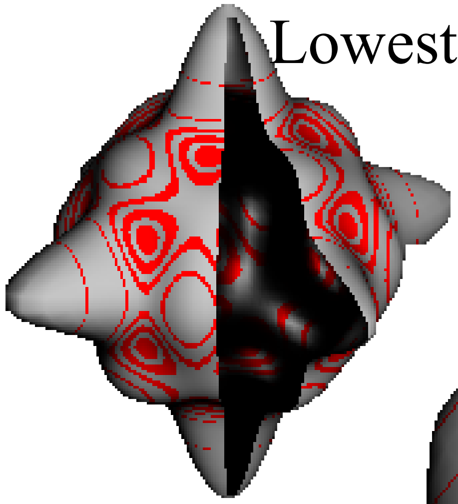


C_1 level clusters

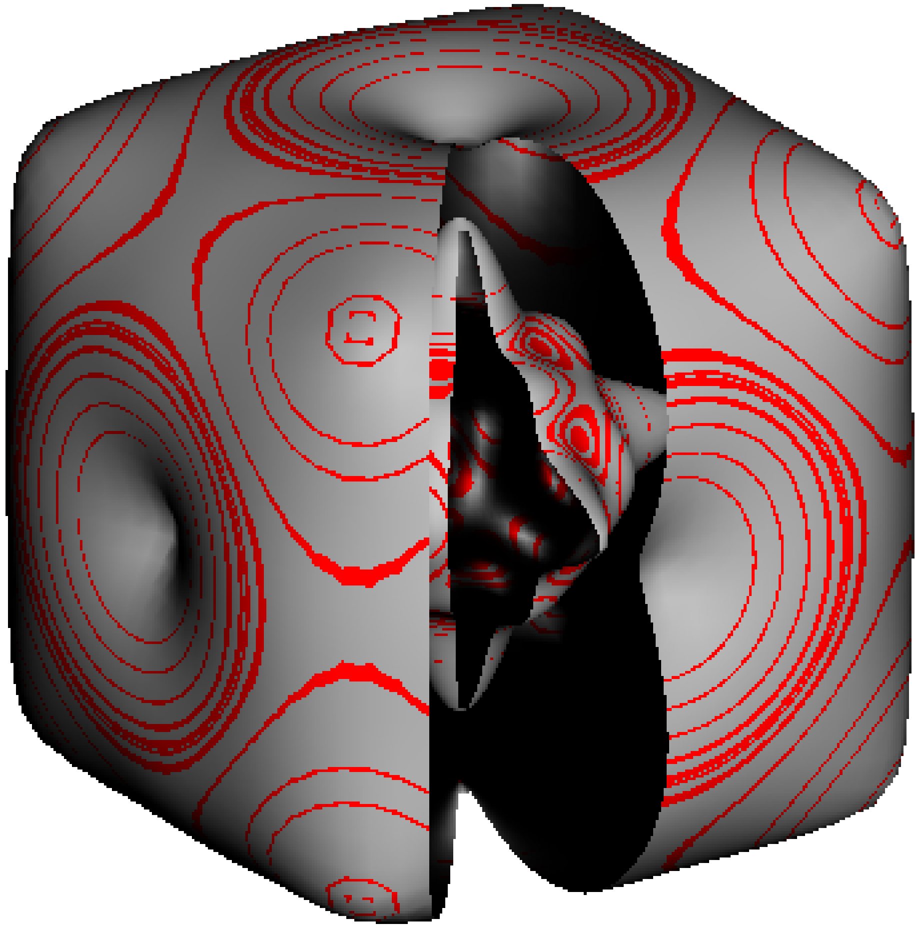
(not seen here.)

ν_3 REES

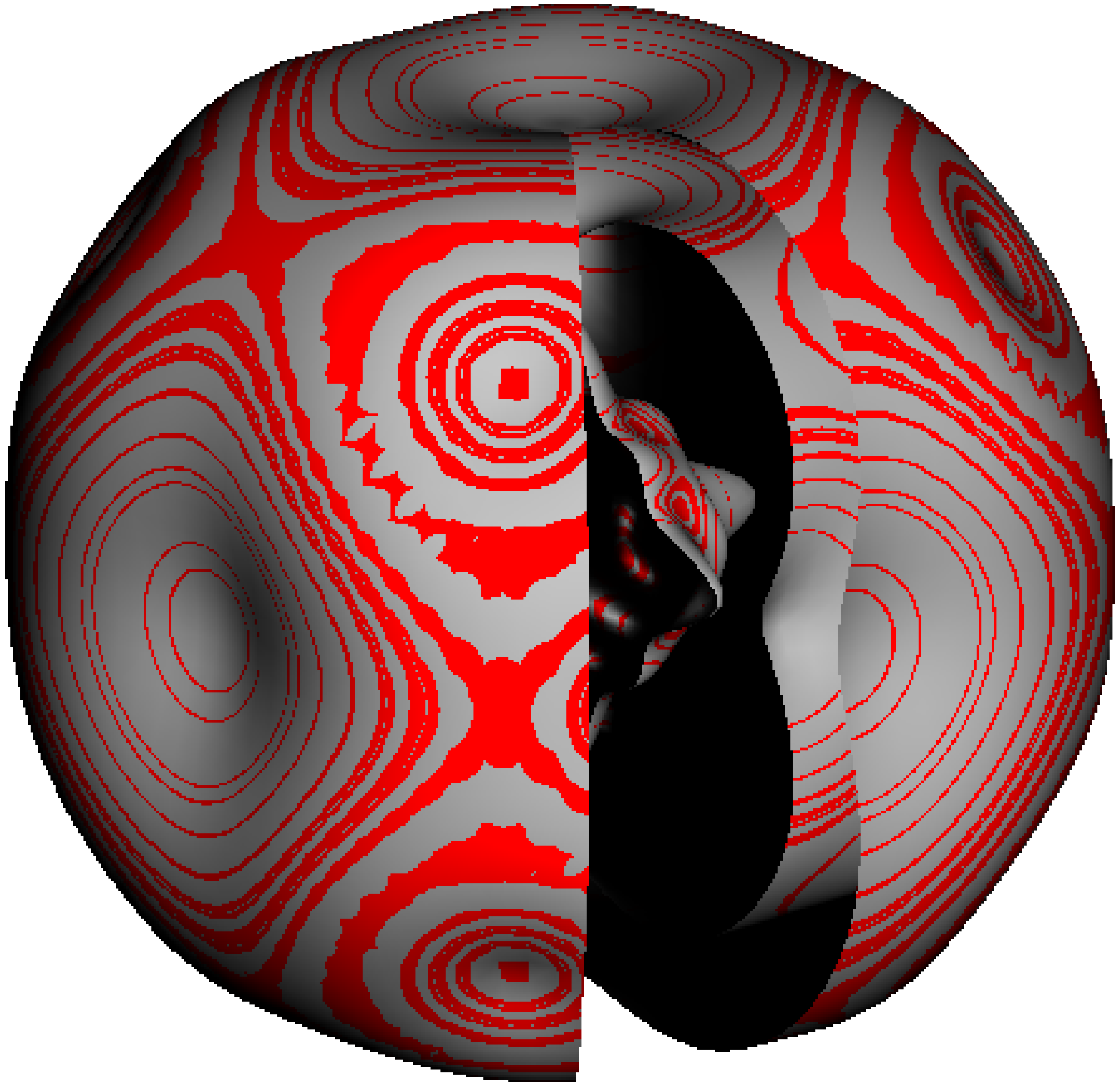




Lowest ν_3 REES



Middle ν_3 REES



Highest ν_3 REES

- *New geometric approach to rotational eigenstates and spectra*
  - *Introduction to Rotational Energy Surfaces (RES) and multipole tensor expansion*
    - *Rank-2 tensors from D^2-matrix*
      - *Building Hamiltonian* $\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2$ *out of scalar and tensor operators*
    - *Comparing quantum and semi-classical calculations*
      - *Symmetric rotor levels and RES plots*
      - *Asymmetric rotor levels and RES plots*
      - *Spherical rotor levels and RES plots*
        - *SF_6 spectral fine structure*
        - ➡ *CF_4 spectral fine structure*

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

W.G.Harter

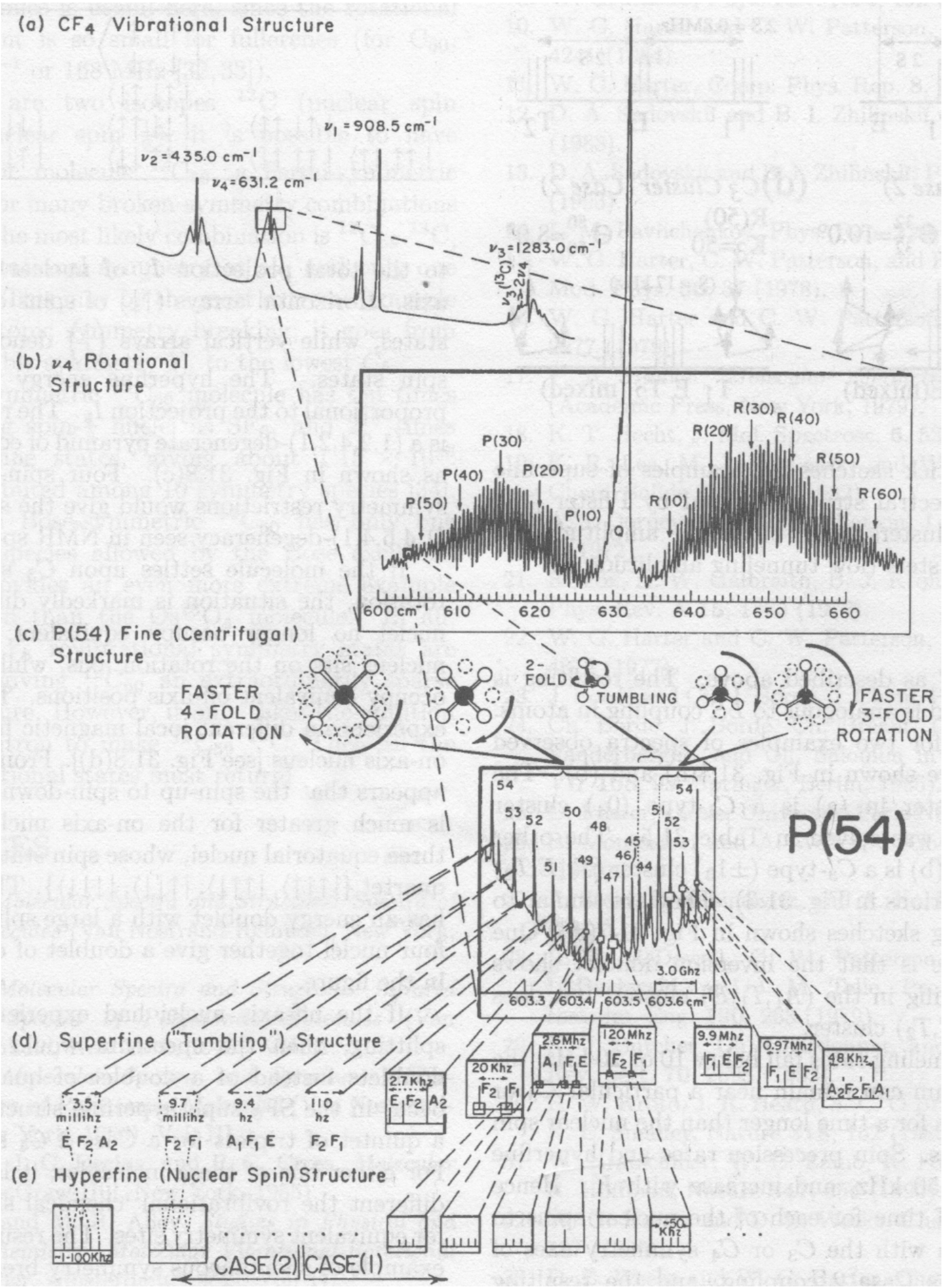
Ch. 31

Atomic, Molecular, & Optical Physics Handbook

Am. Int. of Physics

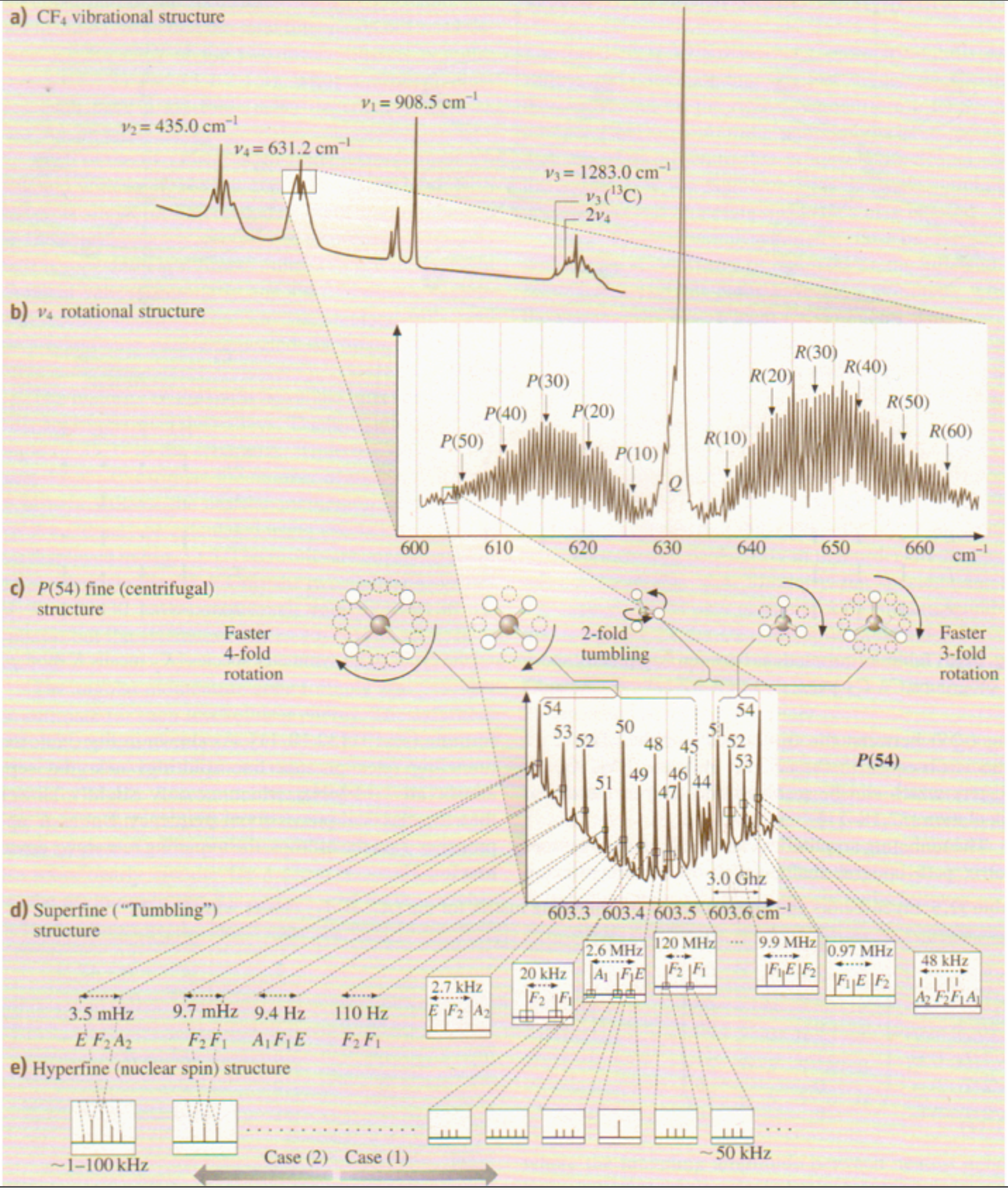
Gordon Drake Editor

(1996)



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

W.G.Harter
Fig. 32.7
Springer Handbook of Atomic, Molecular, & Optical Physics
Gordon Drake Editor (2005)



As of April 3, 2014

Links to the current Harter-Soft LearnIt web apps for Physics

Bold links have default redirect pages. *Italics* are not yet meant for production.Red: the final stages of testing.

List of *production* Harter-Soft Web Apps & Textbooks (For public)

Classical Mechanics with a Bang! - URL is "http://www.uark.edu/ua/modphys/markup/CMwBangWeb.html"
Quantum Theory for the Computer Age - URL is "http://www.uark.edu/ua/modphys/markup/QTCAWeb.html"
LearnIt Web Applications - URL is "http://www.uark.edu/ua/modphys/markup/LearnItWeb.html"

Individual web-apps for current classes:

BohrIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BohrItWeb.html"
BounceIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BounceItWeb.html"
BoxIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/BoxItWeb.html"
CoulIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/CoulItWeb.html"
Cycloidulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/CycloidulumWeb.html"
JerkIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/JerkItWeb.html"
MolVibes - Production; URL is "http://www.uark.edu/ua/modphys/markup/MolVibesWeb.html"
Pendulum - Production; URL is "http://www.uark.edu/ua/modphys/markup/PendulumWeb.html"
QuantIt - Production; URL is "http://www.uark.edu/ua/modphys/markup/QuantItWeb.html"

The old relativity website (2005):
Relativity - Pirelli Entrant - Production; URL is "**http://www.uark.edu/ua/pirelli**" or "http://www.uark.edu/ua/pirelli/html/default.html"

Newer relativity web-apps currently being developed (2013-)
RelativIt Production; URL is "http://www.uark.edu/ua/modphys/markup/RelativItWeb.html"
RelaWavity Production; URL is "http://www.uark.edu/ua/modphys/markup/RelaWavityWeb.html"

Additional classical wep-apps:
Trebuchet Production; URL is "http://www.uark.edu/ua/modphys/markup/TrebuchetWeb.html"
WaveIt Production; URL is "http://www.uark.edu/ua/modphys/markup/WaveItWeb.html"

Link to master list of all Harter-Soft Web Apps & Textbooks (Prod, Testing, & Developement)

http://www.uark.edu/ua/modphys/testing/markup/Harter-SoftWebApps.html