AMOP Lecture 18
Thur. 4.17 2014

Based on QTCA Lectures 24-25
Group Theory in Quantum Mechanics

Introduction to Rotational Eigenstates and Spectra IV

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , QTCA Unit 7 Ch. 21-25)
(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(88) 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

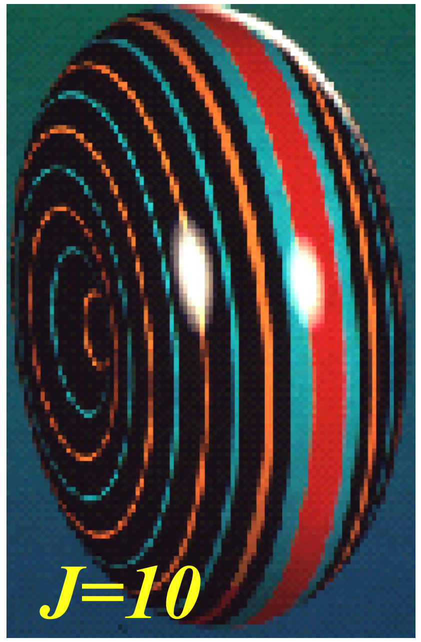
Analogy between PE surface dynamics and RES

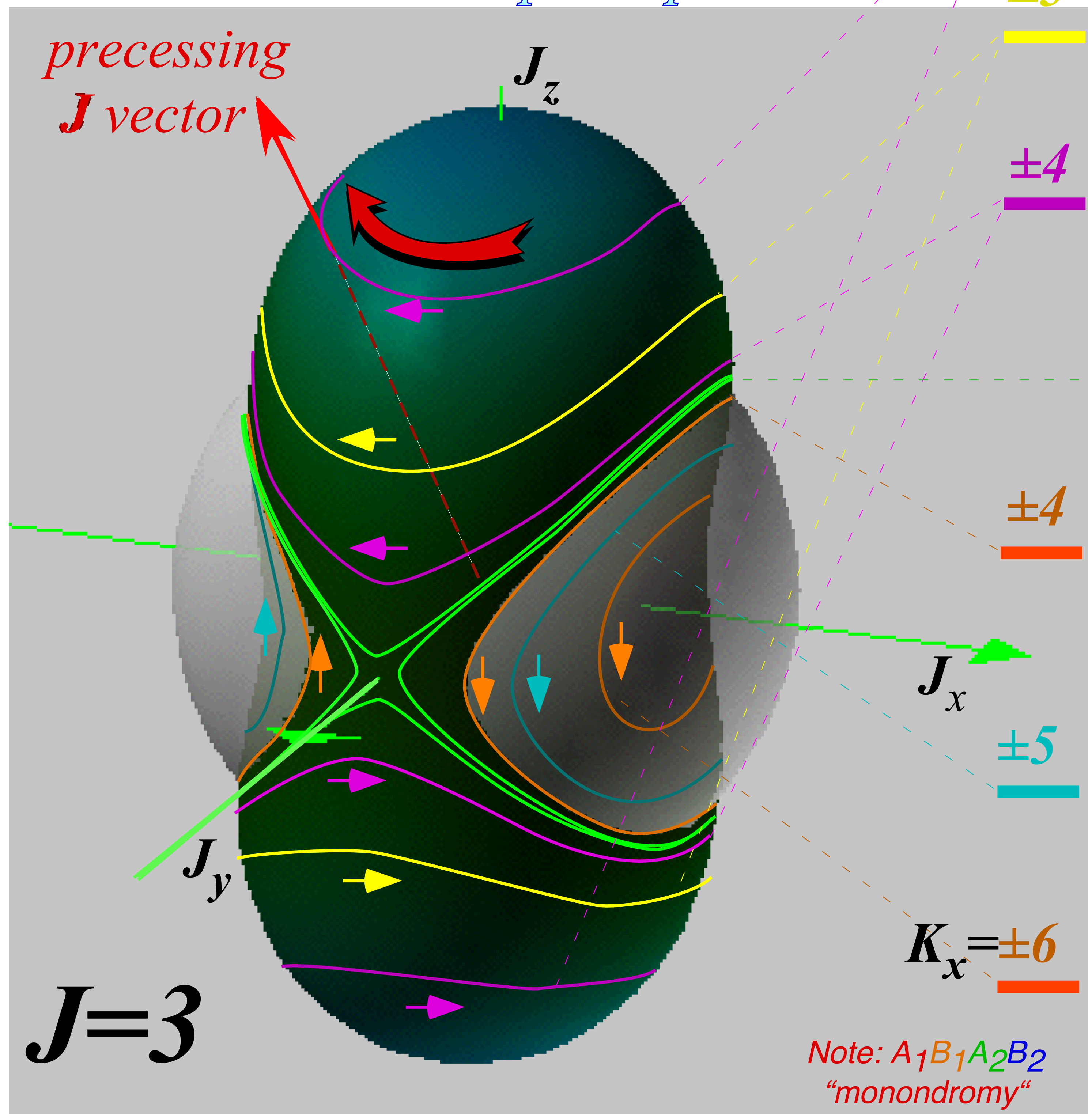
Rotational Energy Eigenvalue Surfaces (REES)

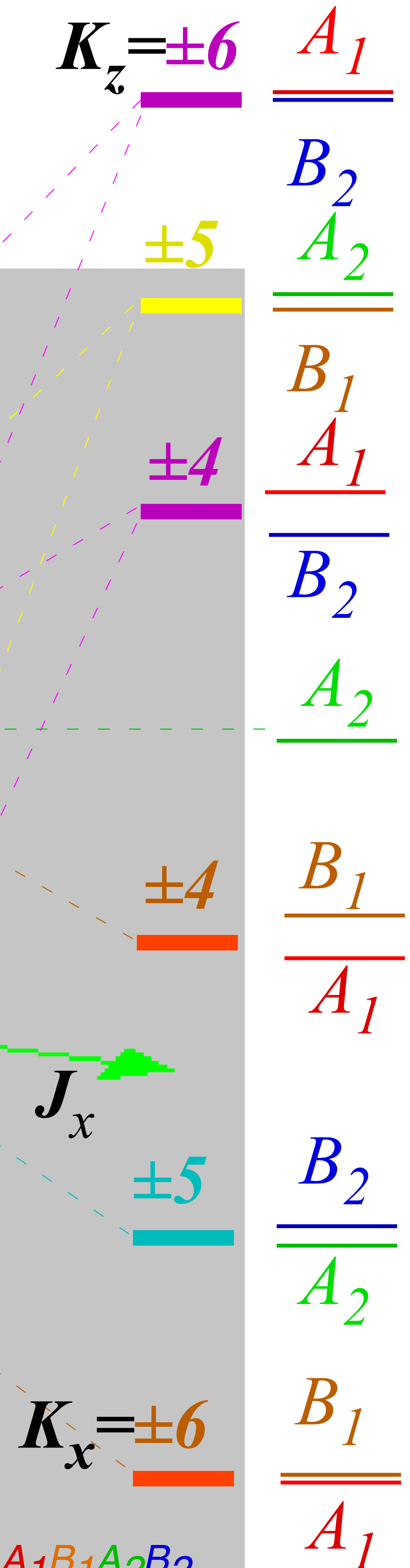
→ *Review:* *Asymmetric rotor levels of* $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *and RES plots*

$D_2 \supset C_2$ symmetry correlation

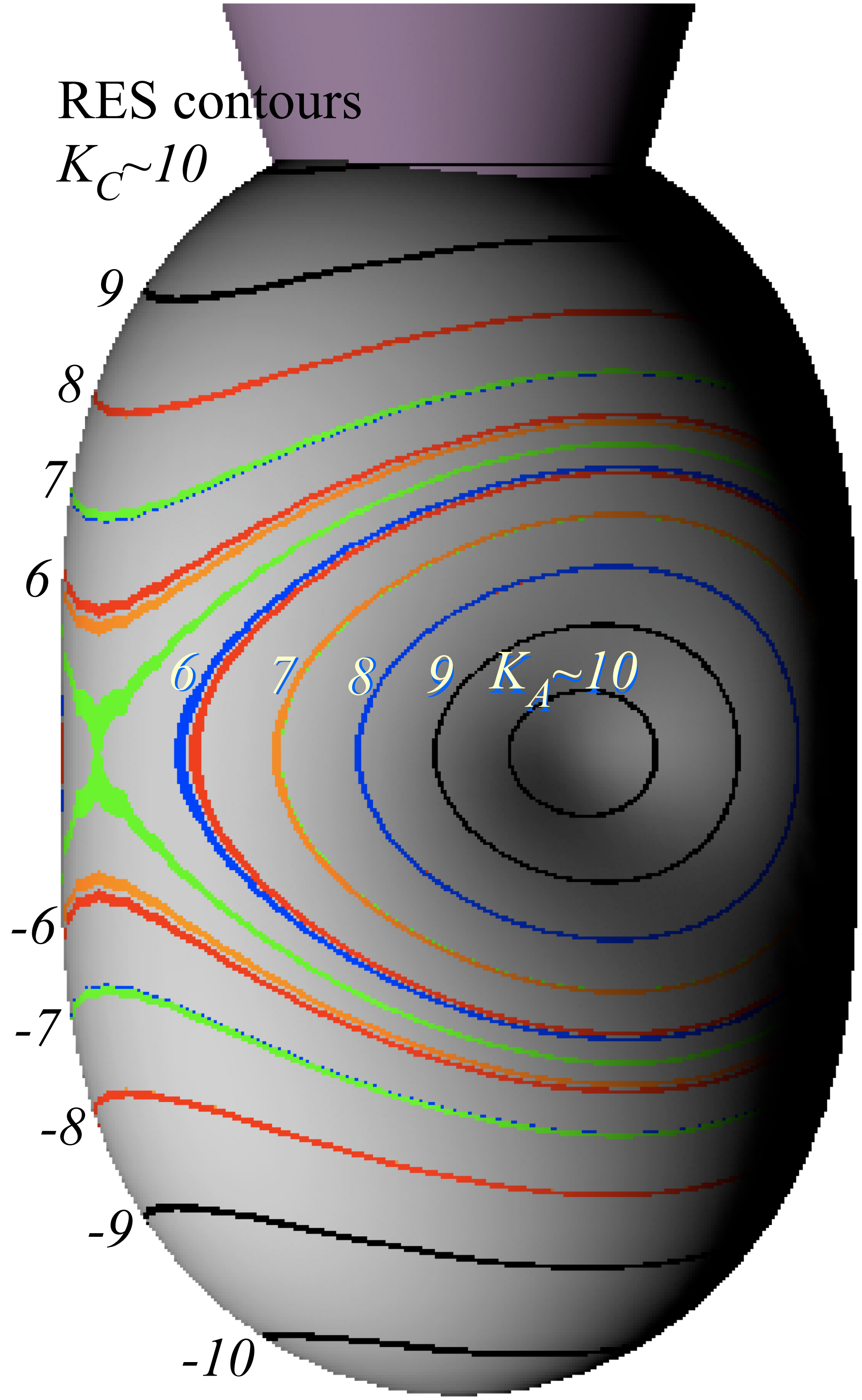
Asymmetric Top Eigensolutions Related to RE Surface and semi-classical J-phase paths





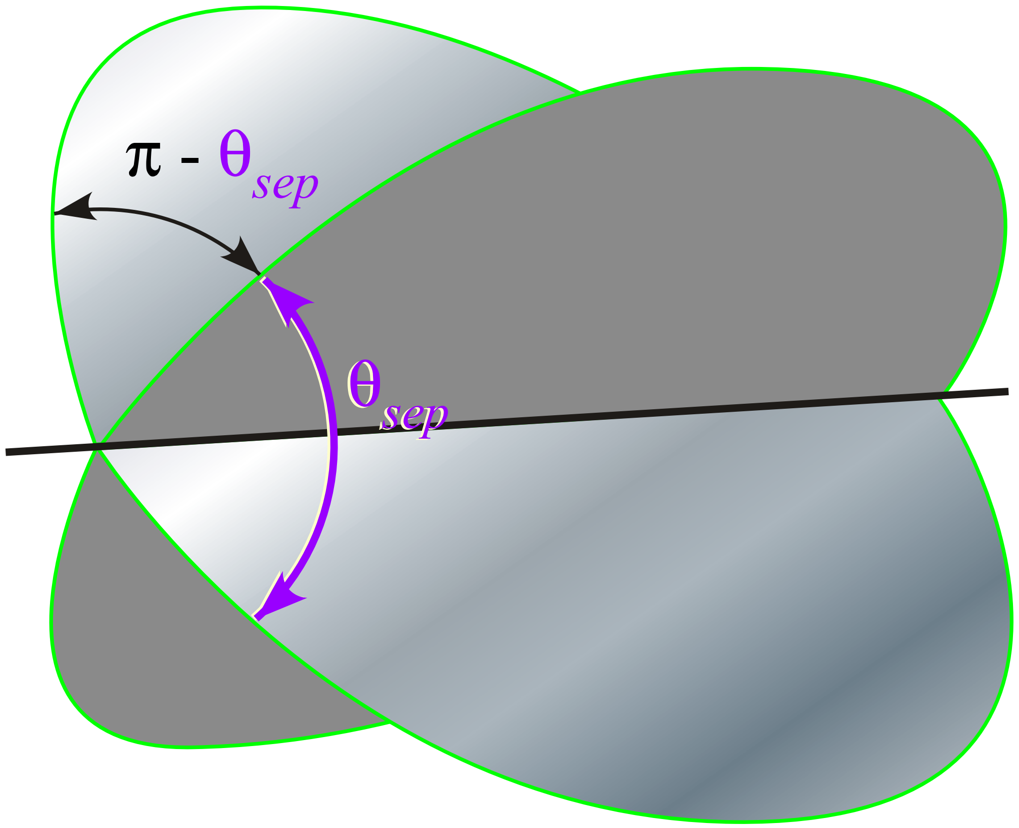


after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

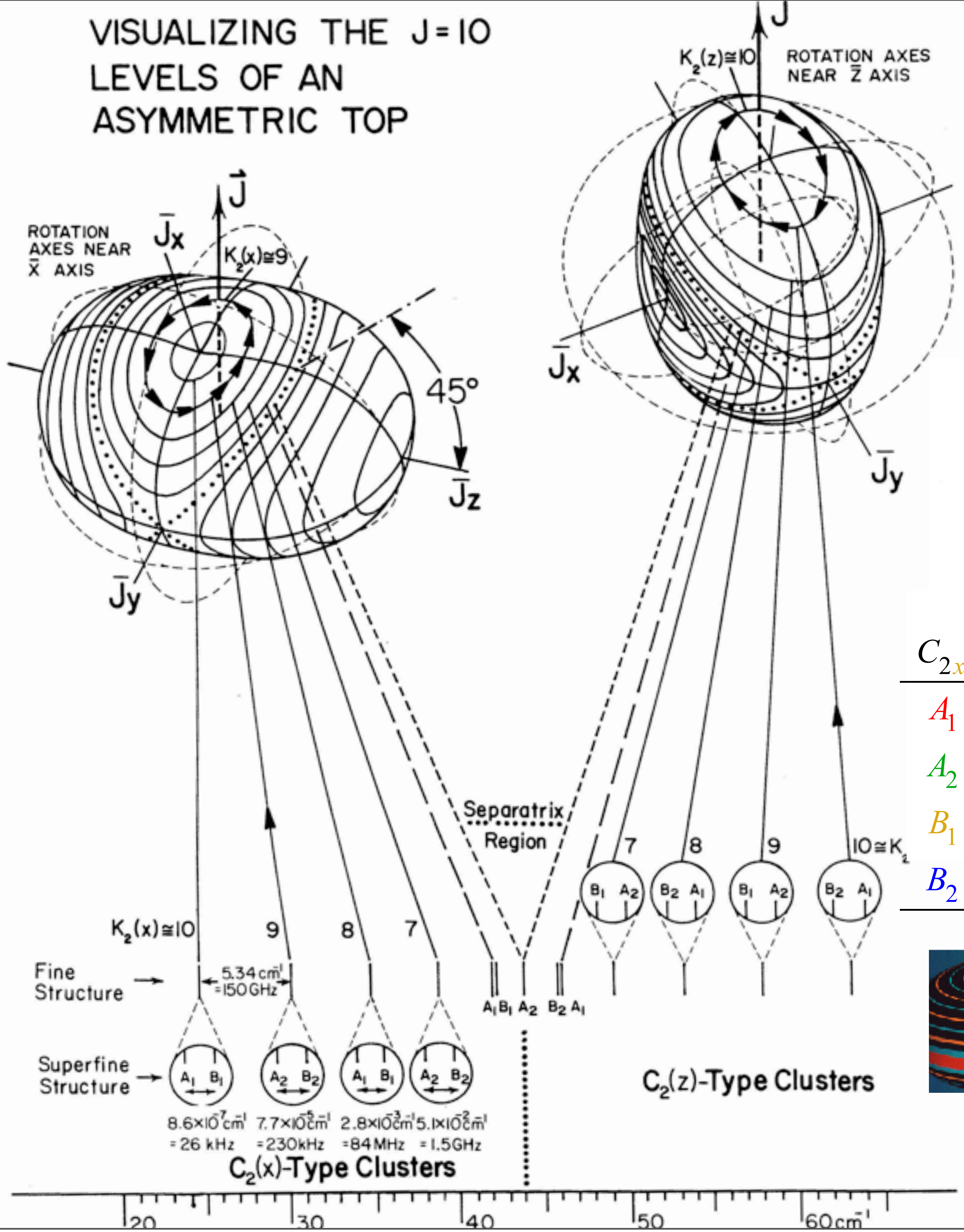


Separatrix circle pair dihedral angle

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



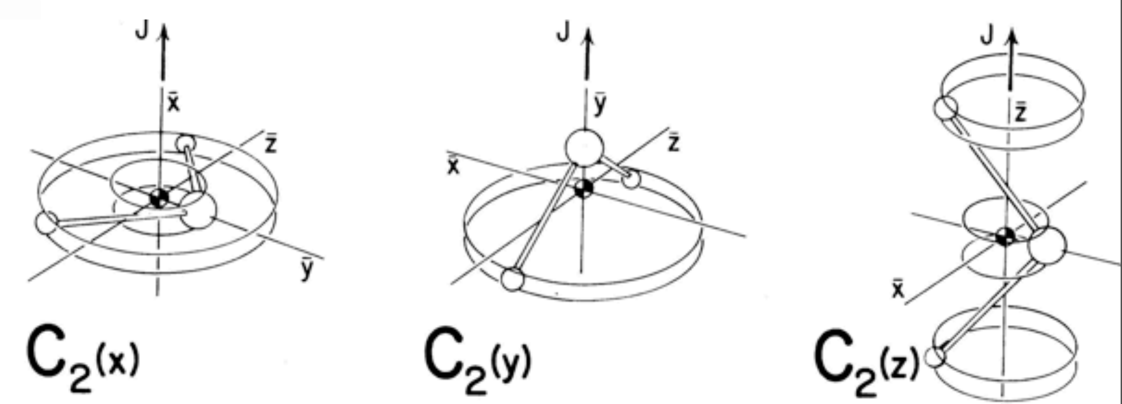
Int.J.Molecular Science 14.(2013) Fig.3 p. 733



D_2	1	R_x	R_y	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	·

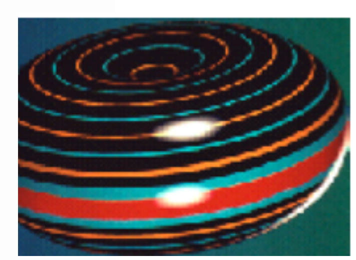


Fig. 25.4.2 *J = 10 asymmetric top energy levels and related RE surface paths (A = 0.2, B = 0.4, C = 0.6). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*

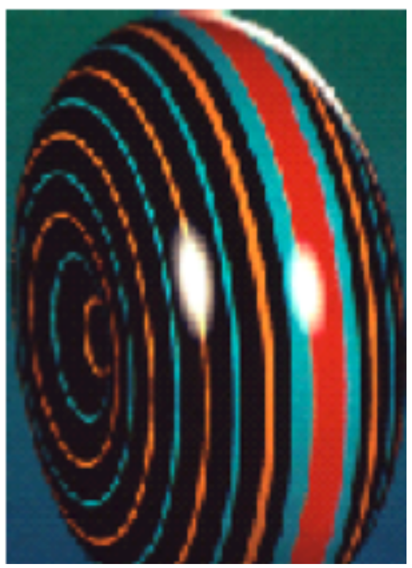
Review: Asymmetric rotor levels of $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *and RES plots*

➡ $D_2 \supset C_2$ *symmetry correlation*

Examples of Group⊃Sub-group correlation

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

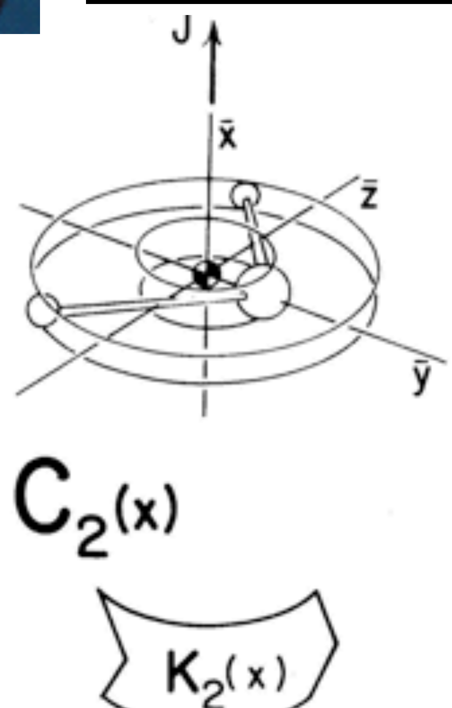
D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

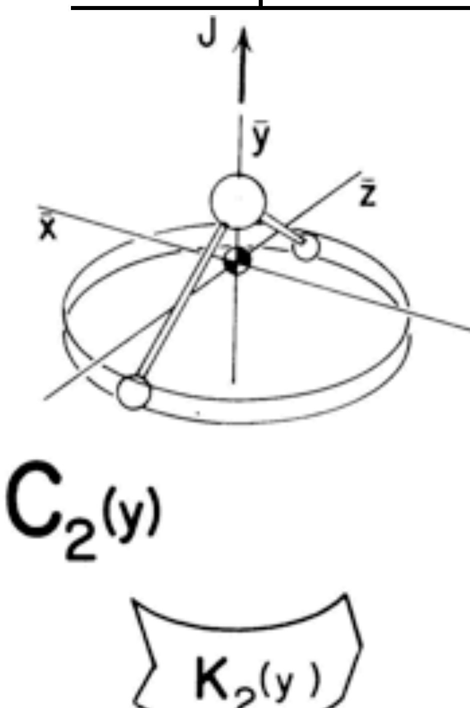


C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

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	·





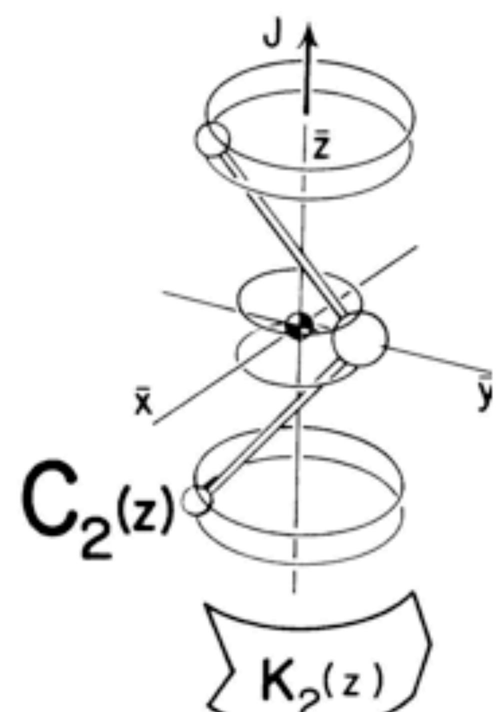
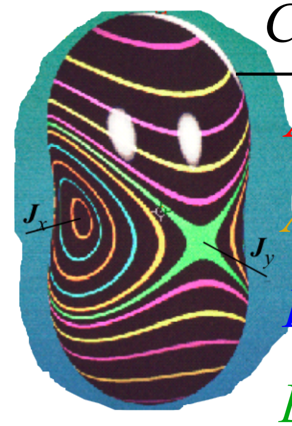


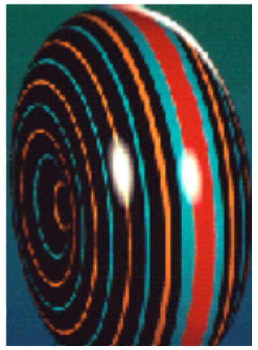
Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*

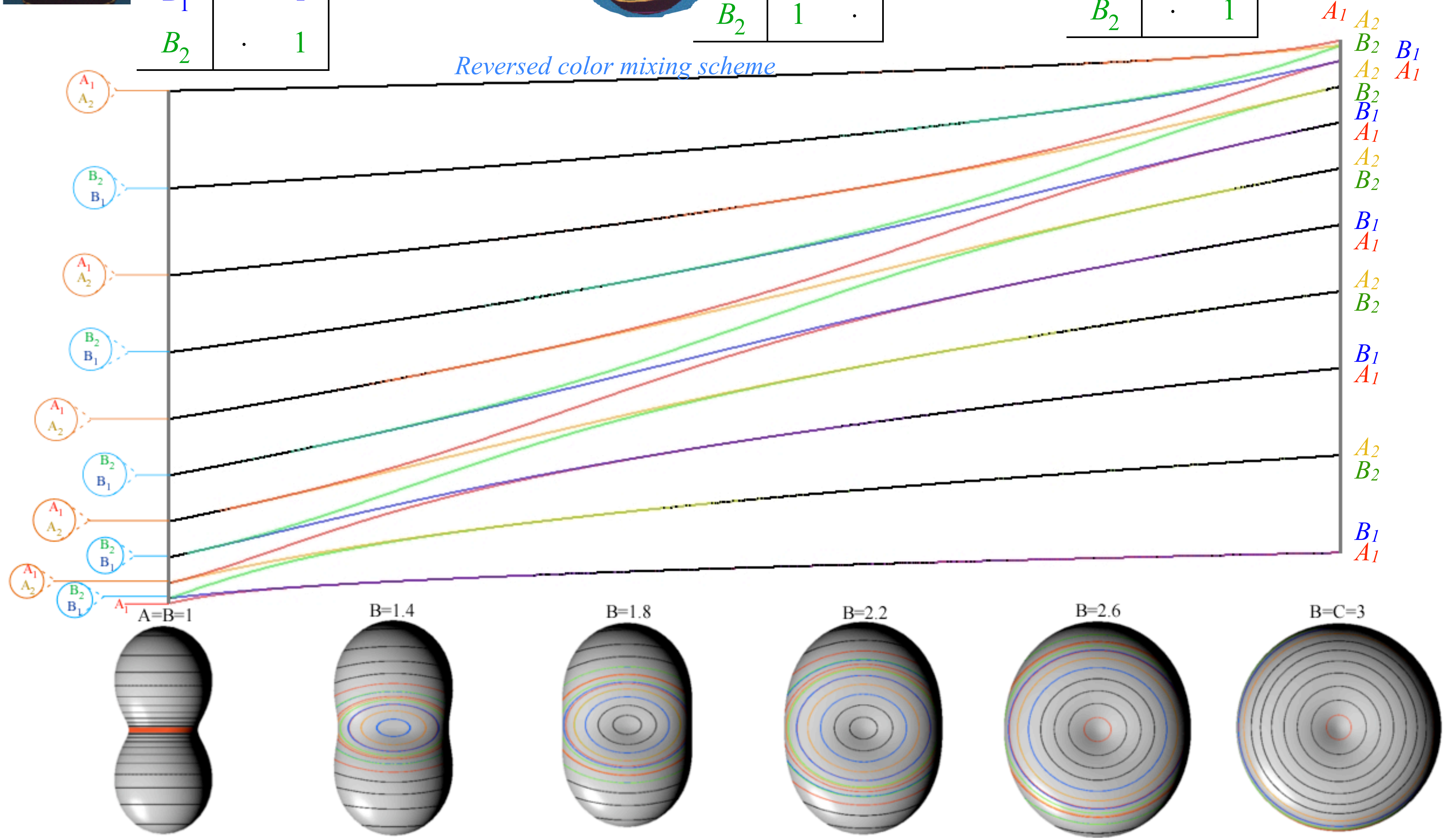
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1



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





(Reversed color mixing scheme used here) *Int.J.Molecular Science 14.(2013)* Fig.4 p. 734

Review: Spherical rotor levels and RES plots

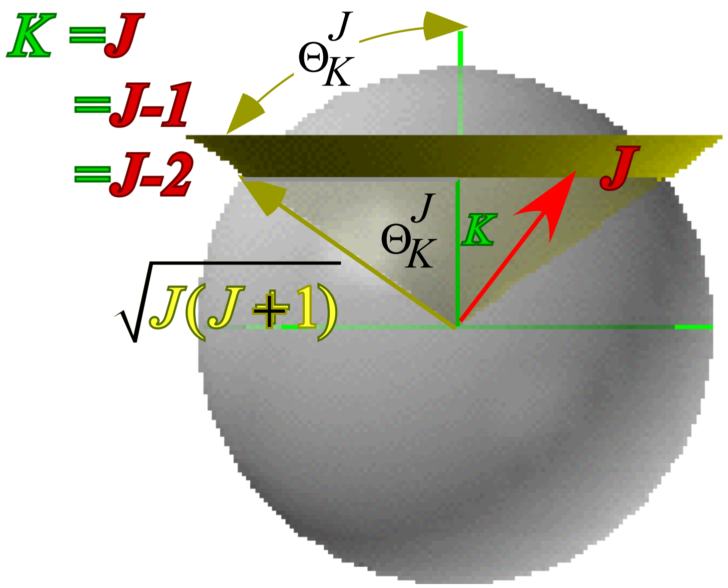
→ *Spectral fine structure of SF_6, SiF_4, C_8H_8,...*

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

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

Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

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

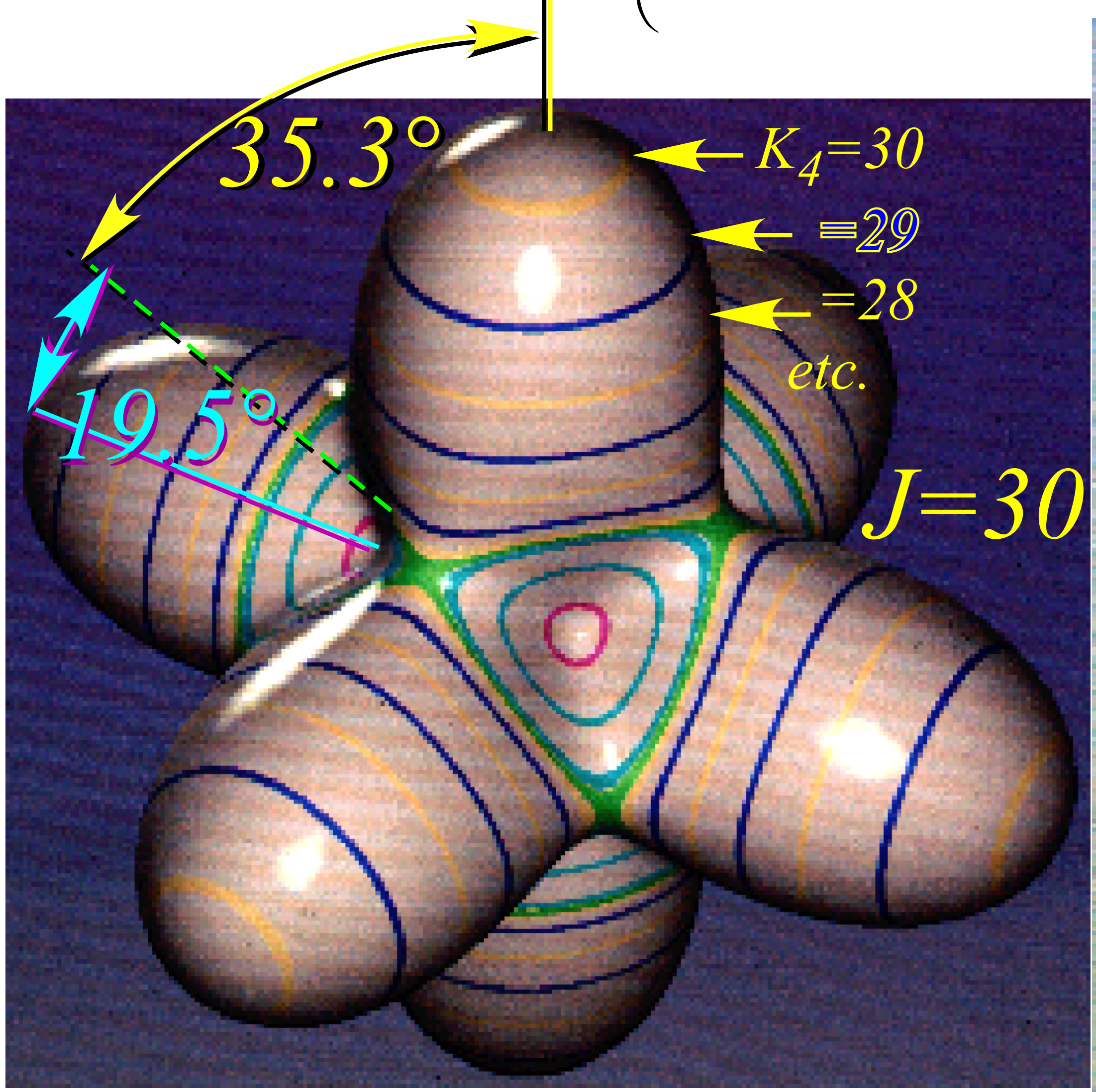


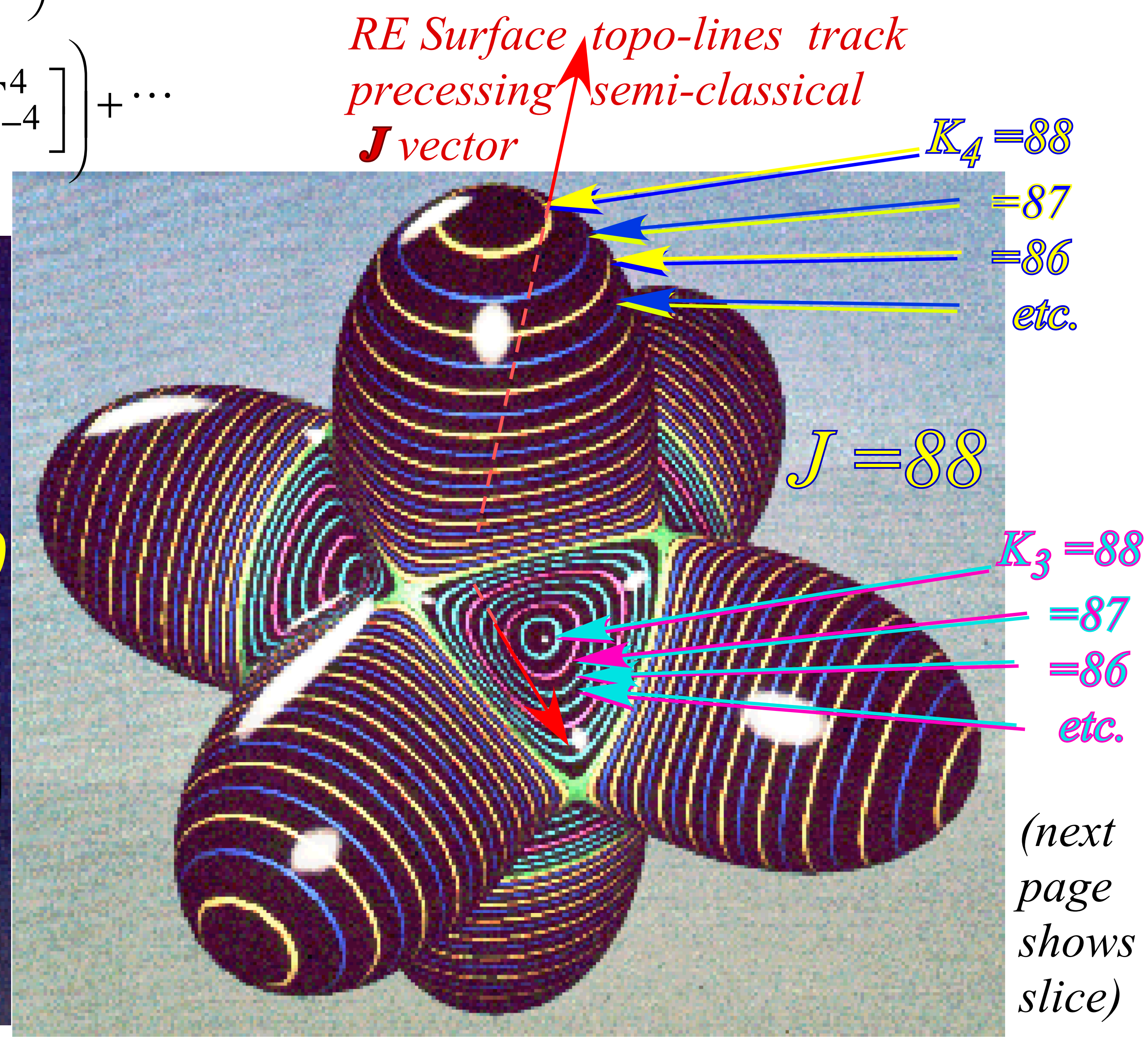
***J** cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels*

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

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

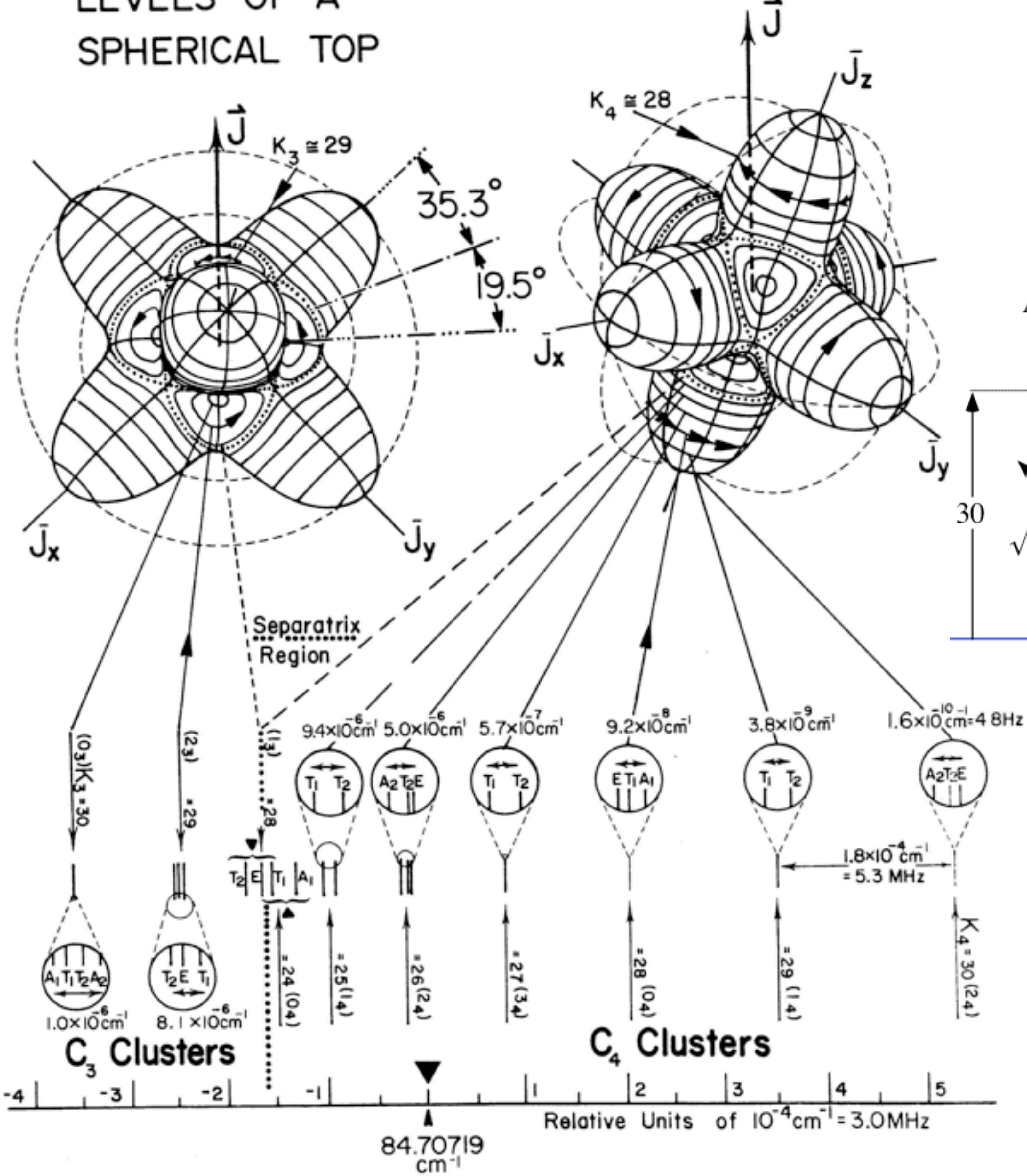
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$

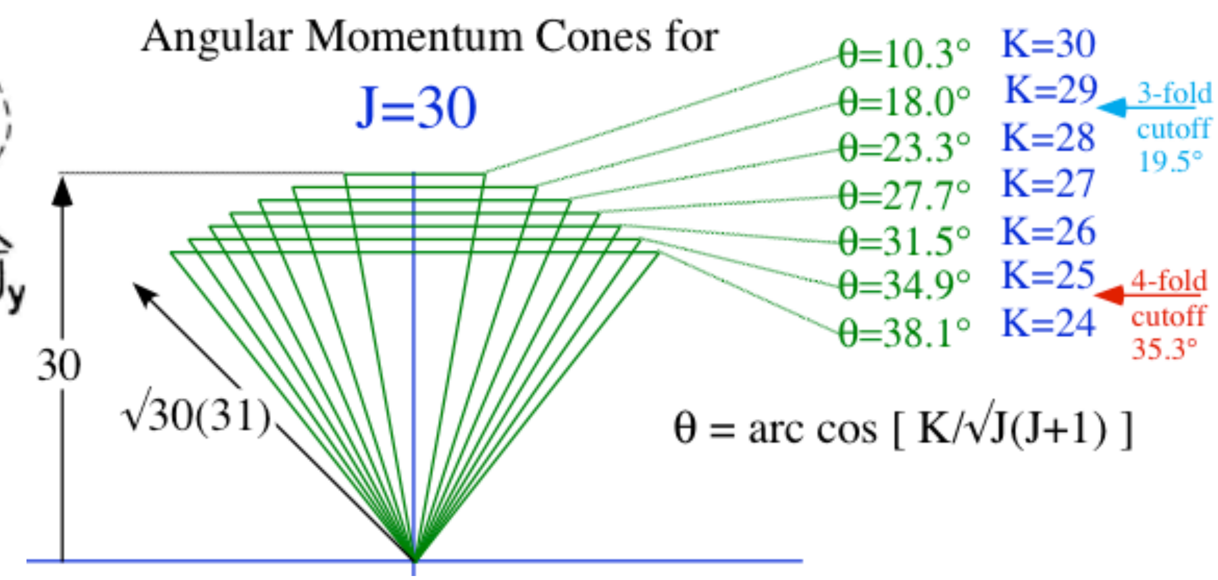




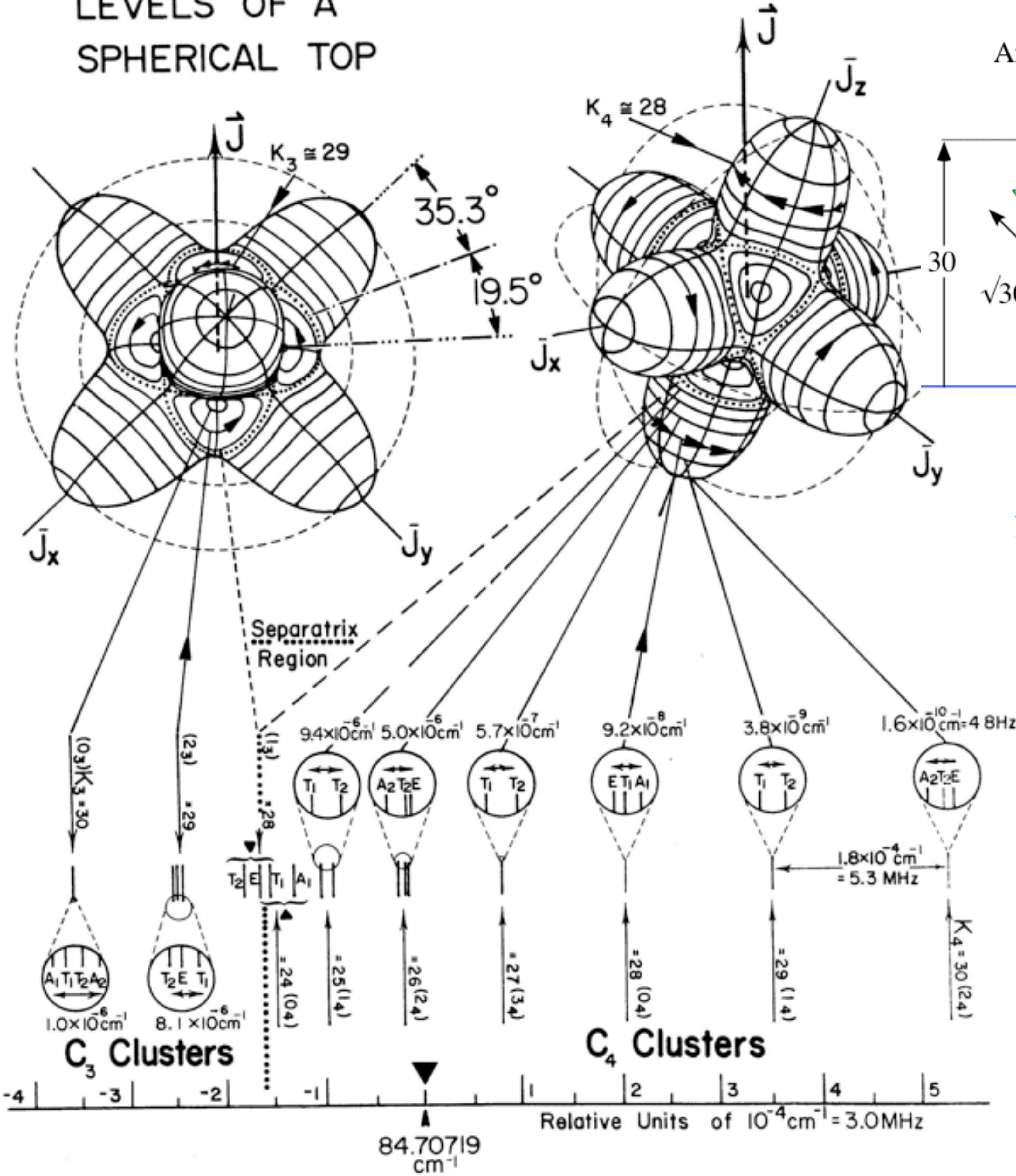
(next page shows slice)

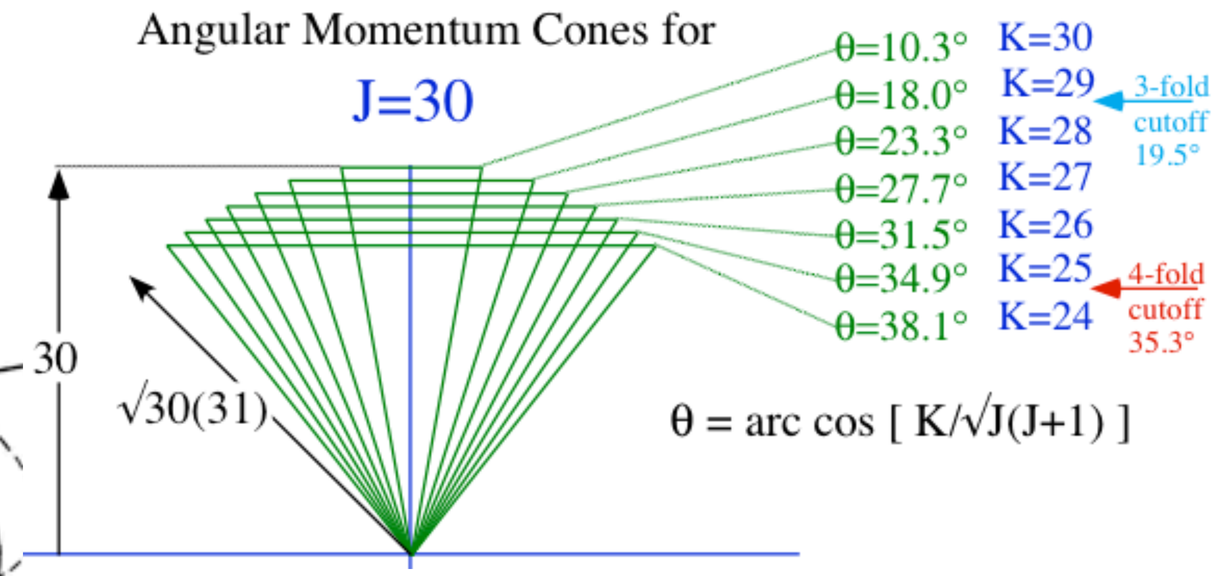
VISUALIZING THE J=30 LEVELS OF A SPHERICAL TOP



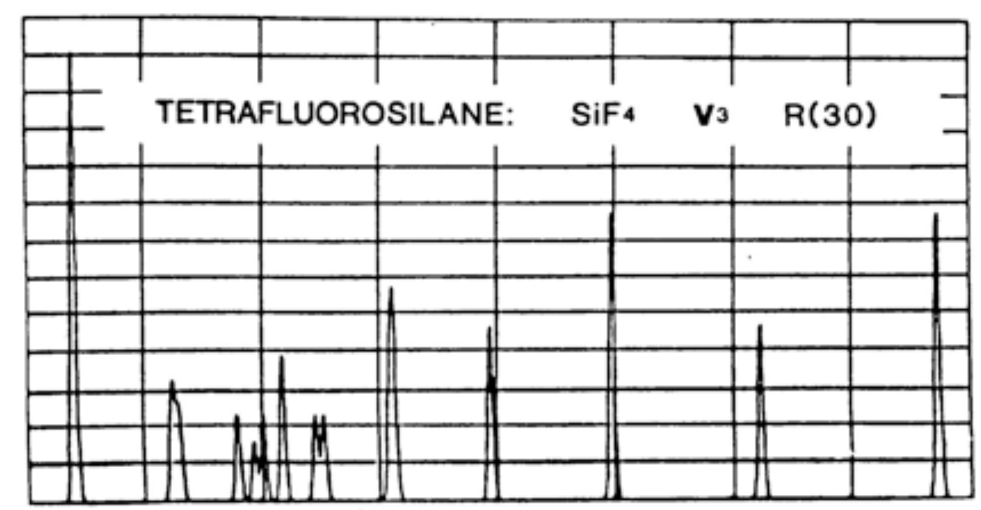


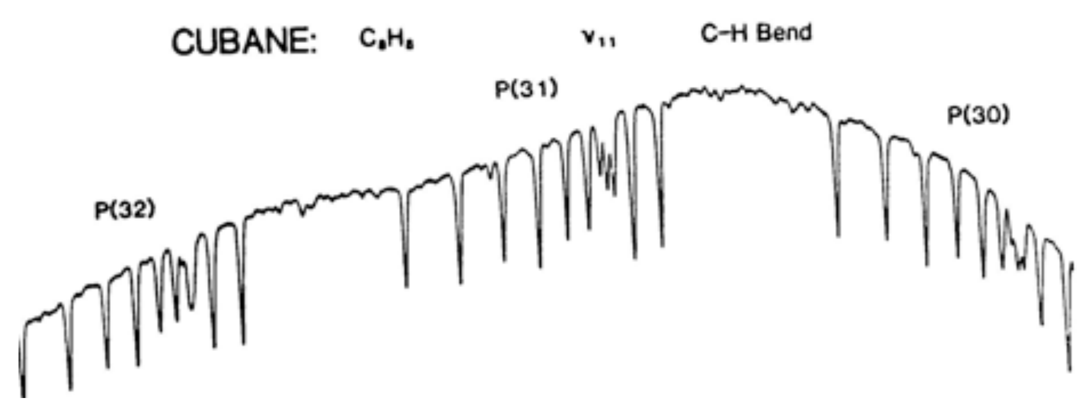
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP





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⊃C₄ subgroup correlations

$\chi_g^\mu(O)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1...4}$	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

$\chi_g^\mu(C_4)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{R}_{z+90°}$	$\mathbf{R}_{z+180°}$	$\mathbf{R}_{z-90°}$
$(0)_4$	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↓C₄ 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⊃C₃ subgroup correlations

$\chi_g^\mu(O)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1...4}$	$\boldsymbol{\rho}_{xyz}$	$\mathbf{R}_{xyz}$	$\mathbf{i}_{1...6}$
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

$\chi_g^\mu(C_3)$	$\mathbf{g}=\mathbf{1}$	$r_{z+120°}$	$r_{z-120°}$
$(0)_3$	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↓C₃ subduction

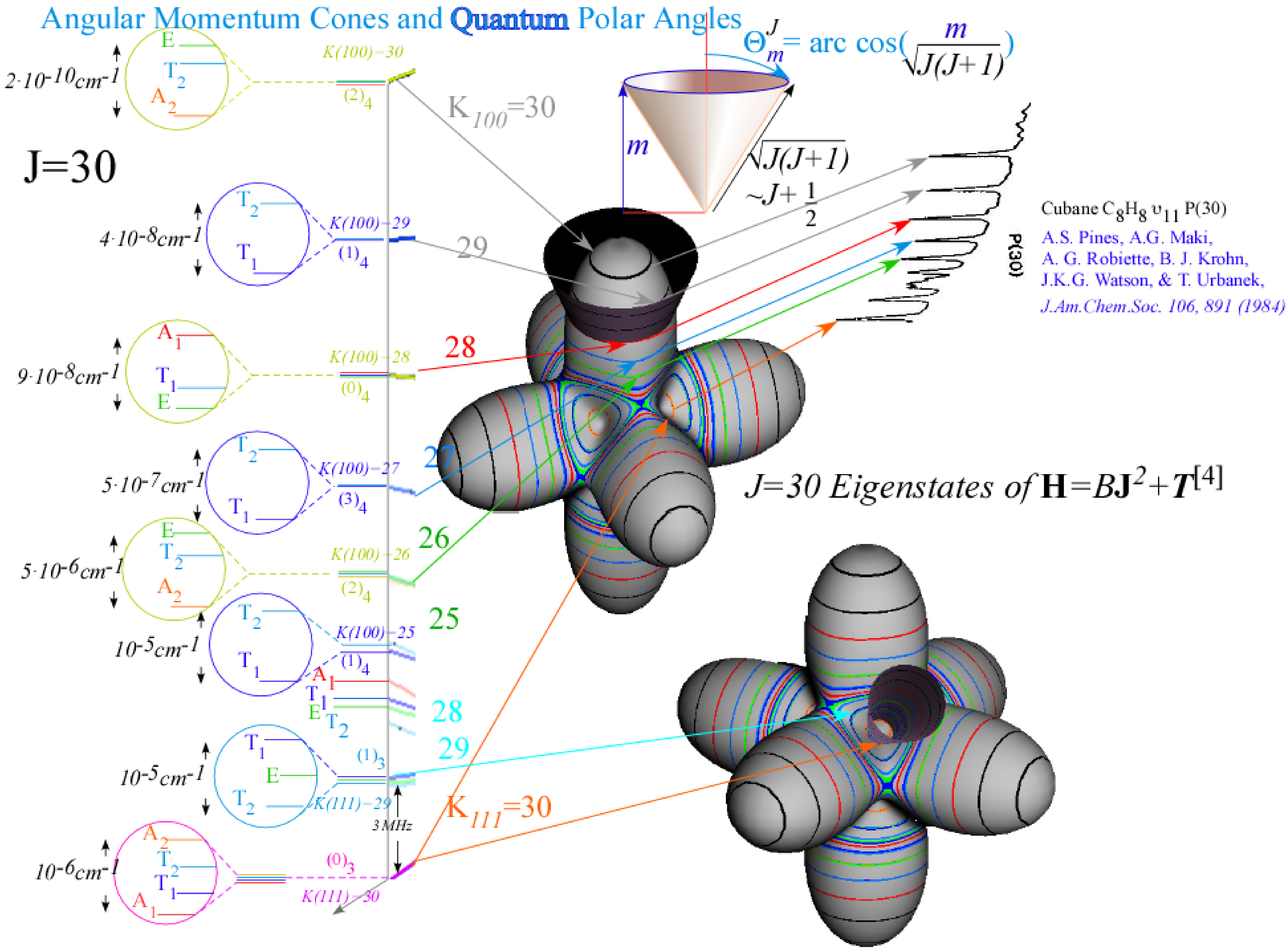
$O\downarrow C_3$	0_3	1_3	$2_3=\bar{1}_3$
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

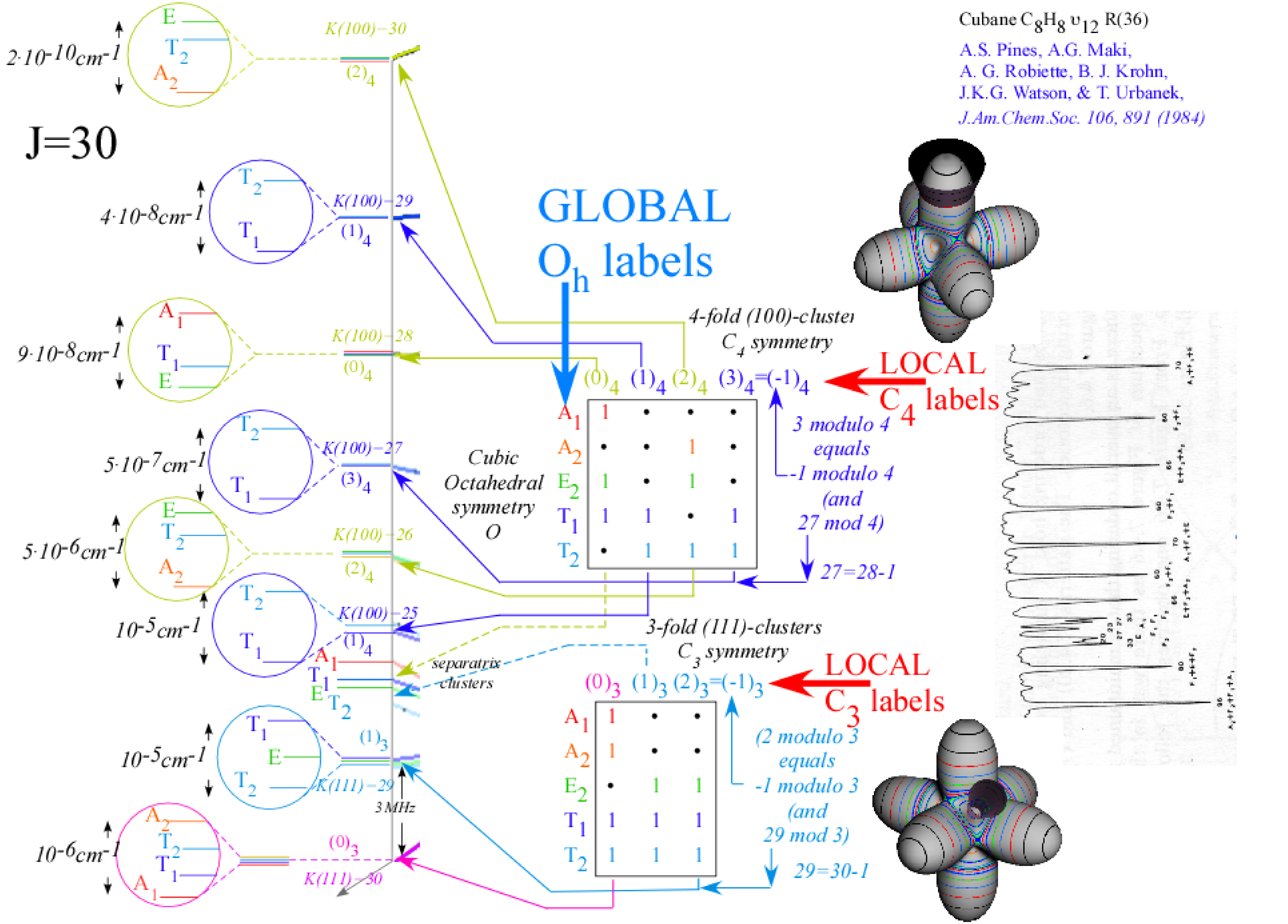
Review: Spherical rotor levels and RES plots

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)*

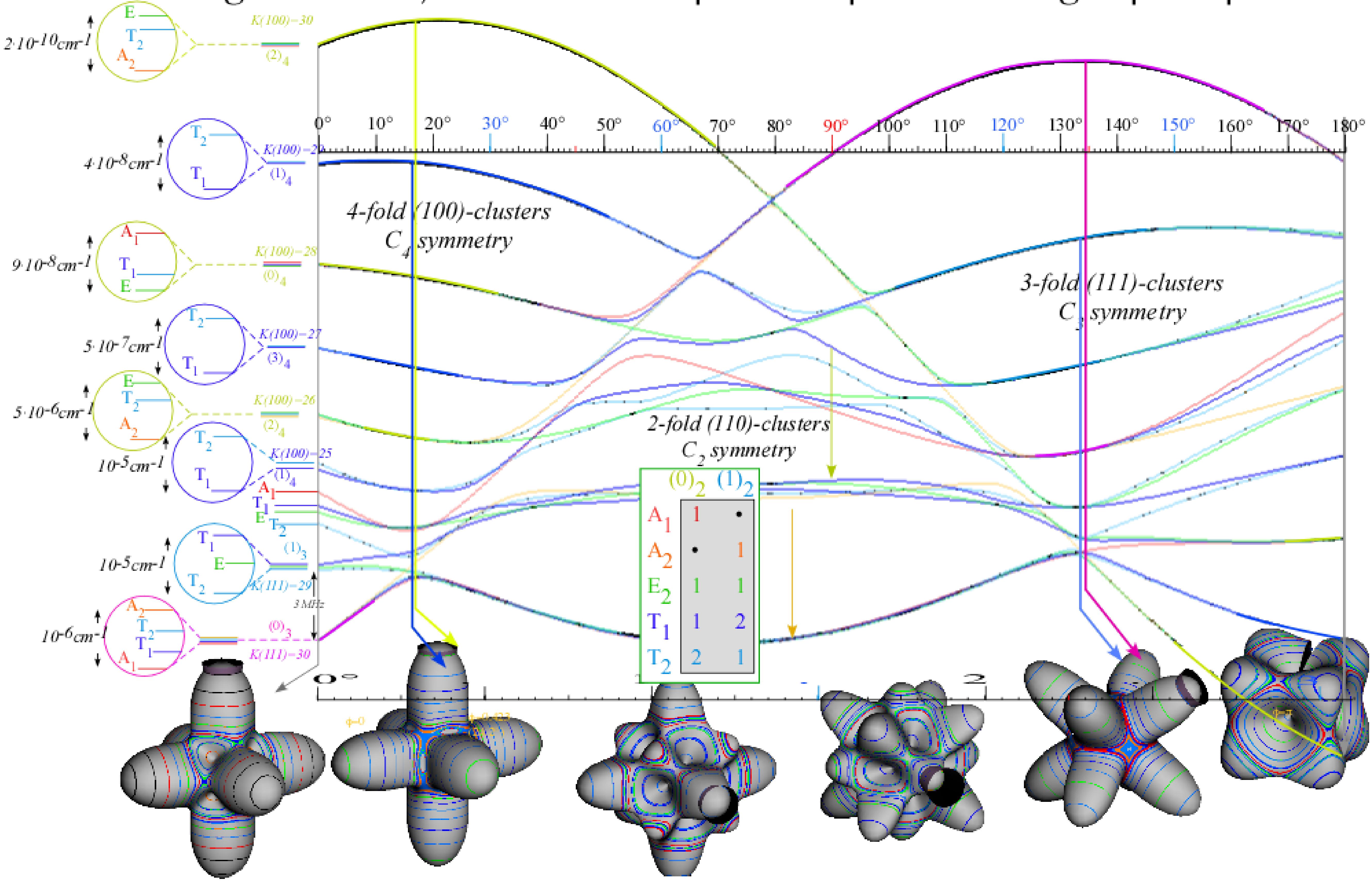

Angular Momentum Cones and Quantum Polar Angles
$\Theta_m^J = \arccos\left(\frac{m}{\sqrt{J(J+1)}}\right)$
m
$\sqrt{J(J+1)}$
$\sim J+\frac{1}{2}$
J=30
K_{100}=30
29
28
27
26
25
28
29
K_{111}=30
$2\cdot10^{-10}cm^{-1}$
$4\cdot10^{-8}cm^{-1}$
$9\cdot10^{-8}cm^{-1}$
$5\cdot10^{-7}cm^{-1}$
$5\cdot10^{-6}cm^{-1}$
$10^{-5}cm^{-1}$
$10^{-5}cm^{-1}$
$10^{-6}cm^{-1}$
K(100)=30
K(100)=29
K(100)=28
K(100)=27
K(100)=26
K(100)=25
K(111)=29
K(111)=30
3 MHz
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)
P(30)
J=30 Eigenstates of $\mathbf{H}=B\mathbf{J}^2+T^{[4]}$



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

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

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) ν_4 SF_6 and P(88) ν_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>

	<u>Example(s)</u>
Introductory review	
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and θ_K^J-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) ν_4 SF_6 and P(88) ν_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.)

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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

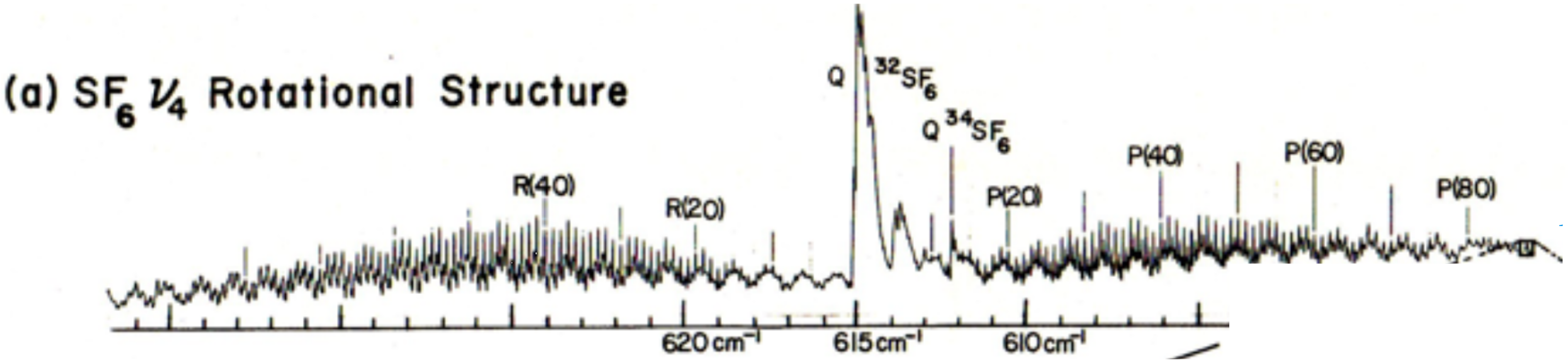
Introductory review

Example(s)

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



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"

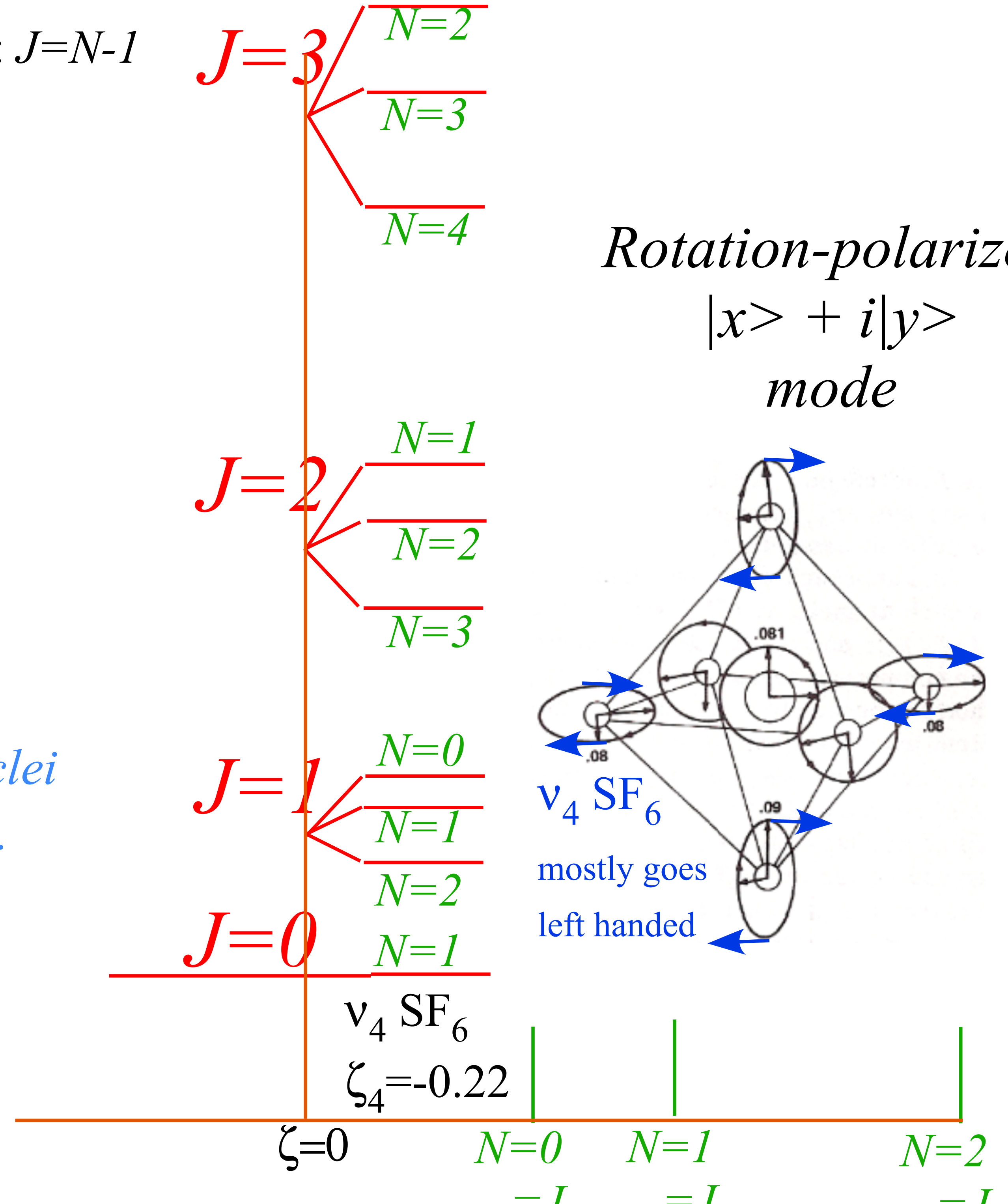
angular momentum **N** *(or* **R***) of rotating nuclei*

total momentum **J** $=\ell+$**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
$|x\rangle + i|y\rangle$
mode

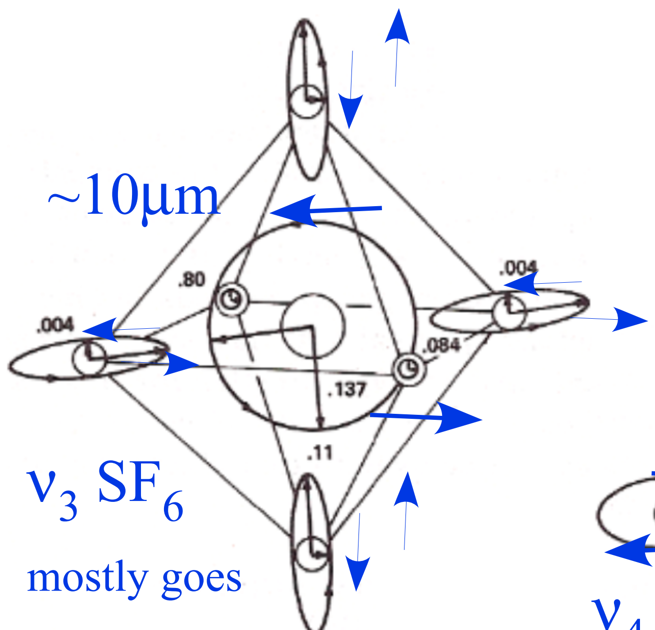


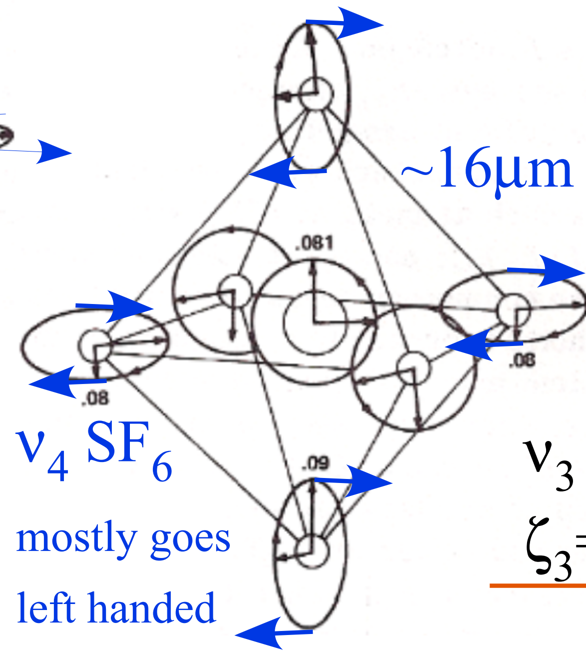
$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

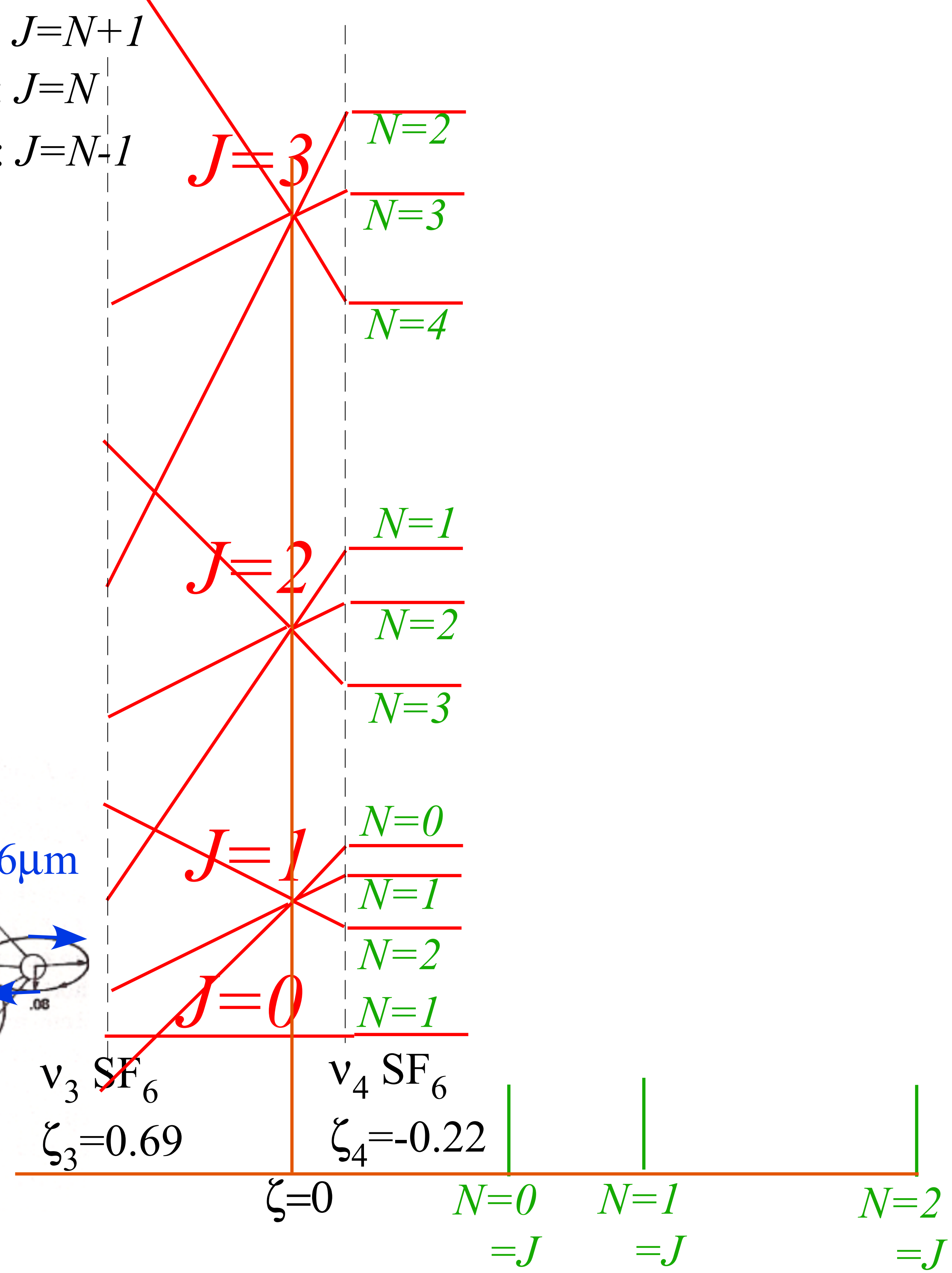
$$\langle H\rangle \sim \nu_{vib} + BN(N+1) + 2B(1-\zeta)\cdot\begin{cases} N+1 & \text{for : } J=N+1 \\ 0 & \text{for : } J=N \\ N & \text{for : } J=N-1 \end{cases}$$

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

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







Details of P(88) ν_4 SF_6 and P(88) ν_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)

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

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

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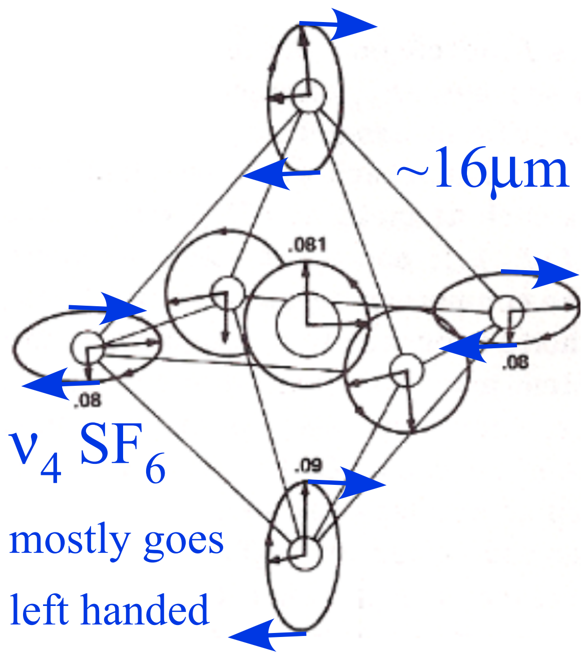
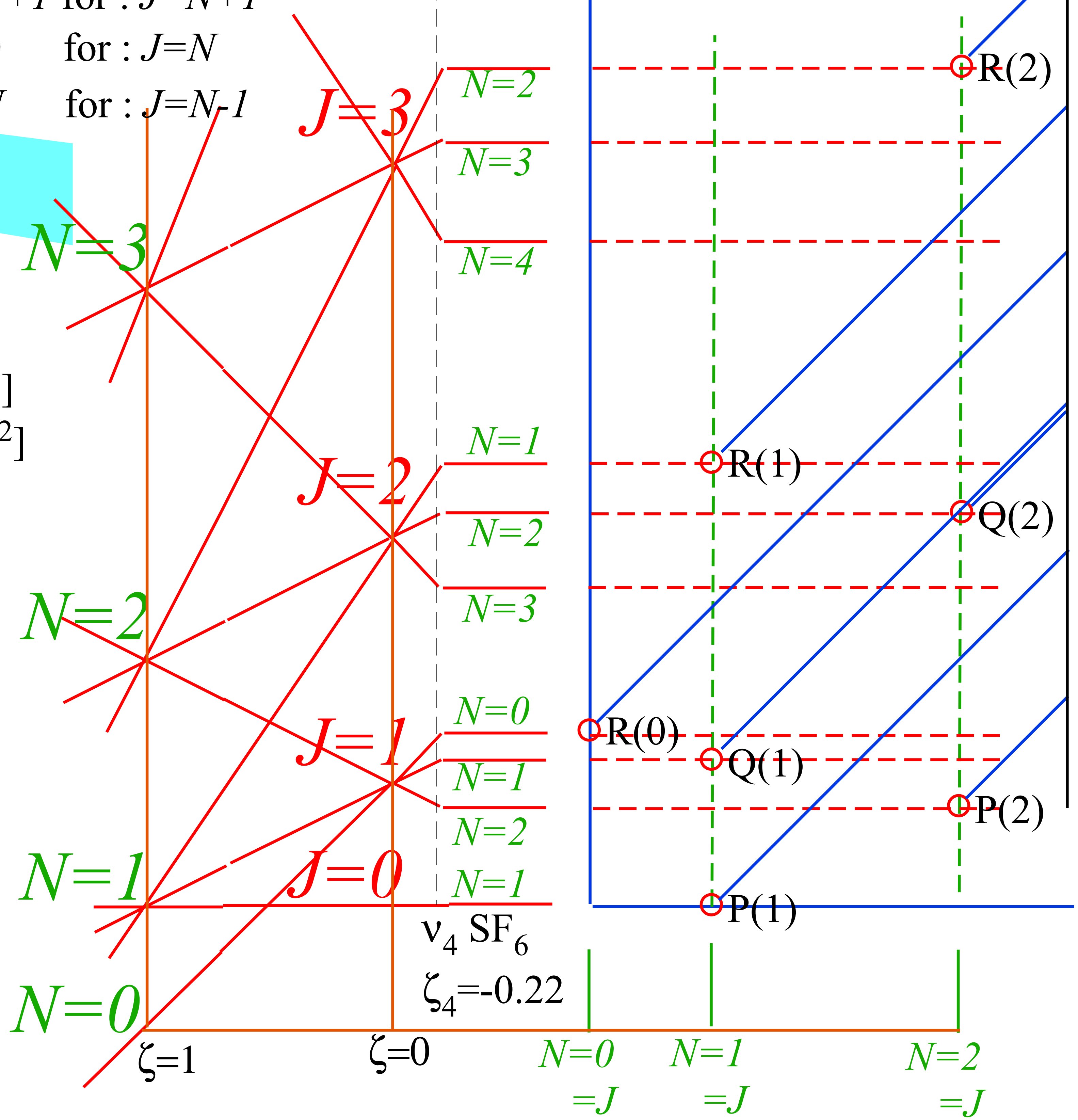
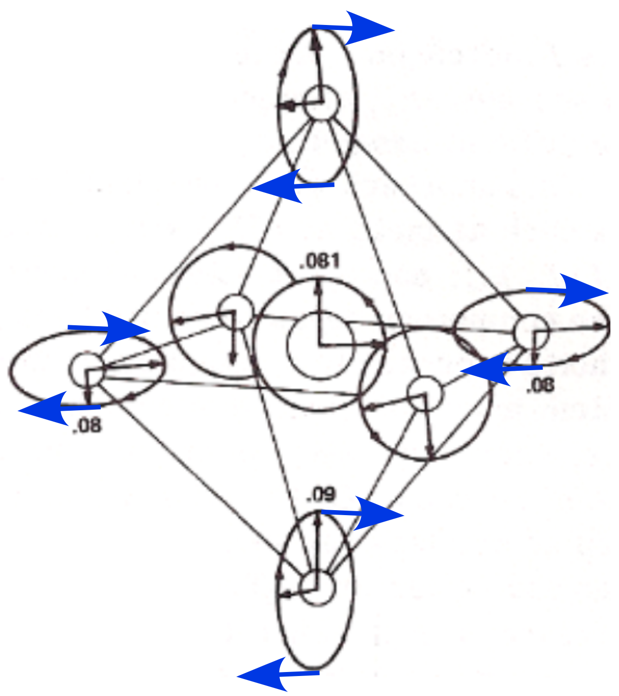


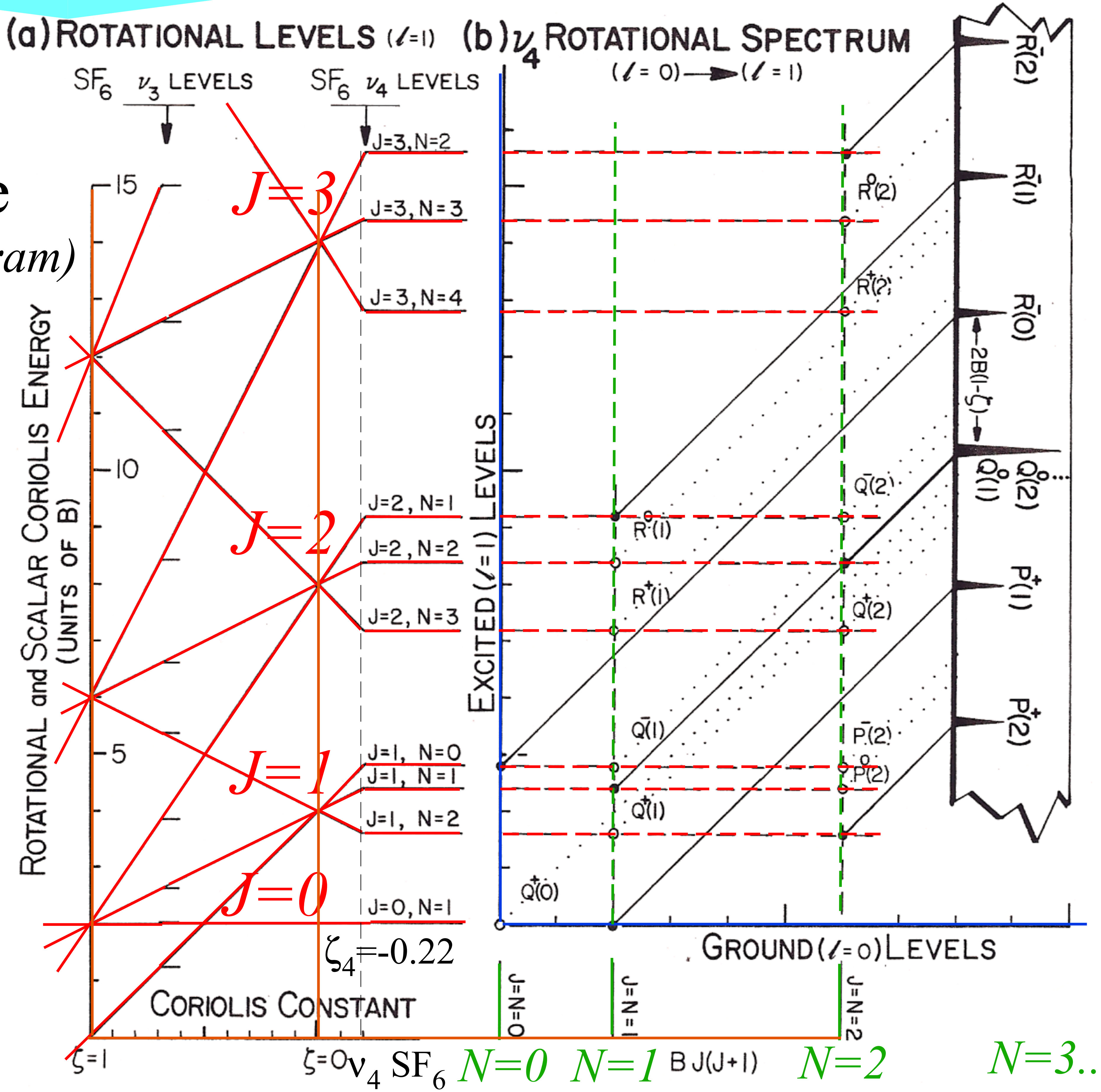


$\langle H \rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis} \rangle + \langle H^{Tensor\ Centrifugal} \rangle + \langle H^{Tensor\ Coriolis} \rangle + \langle H^{Nuclear\ Spin} \rangle + \ldots$

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

(Using rovib. nomogram)





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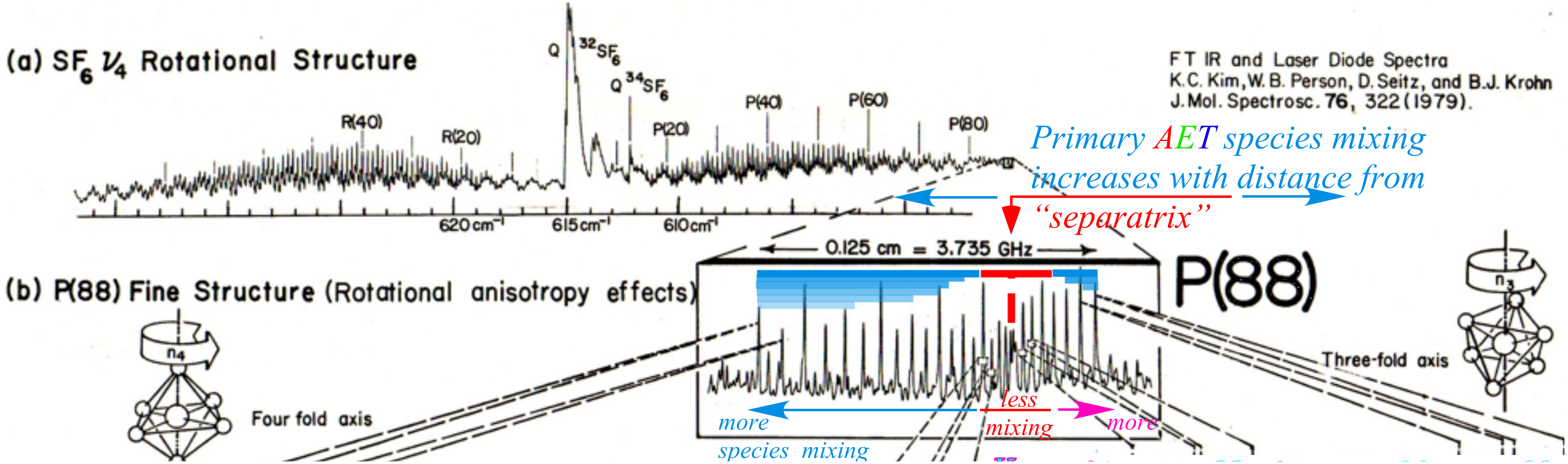


PQR structure due to Coriolis scalar interaction between vibrational angular momentum ℓ and total momentum **J** *=ℓ+***N** *of rotating nuclei*

P(N)=P(88) structure due to tensor centrifugal/Coriolis due to vibrational ℓ and total momentum **J** *=ℓ+***N**

Graphical approach to rotation-vibration-spin Hamiltonian

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

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

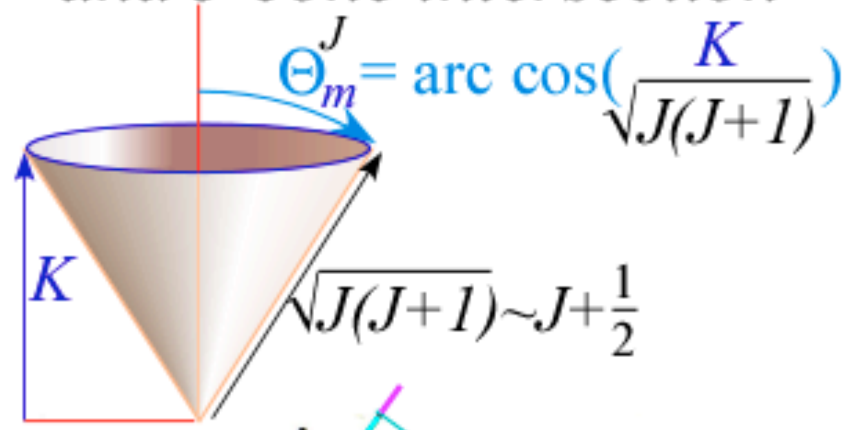
- *Analogy between PE surface and RES dynamics*
- *Rotational Energy Eigenvalue Surfaces (REES)* — ν_3 SF_6

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

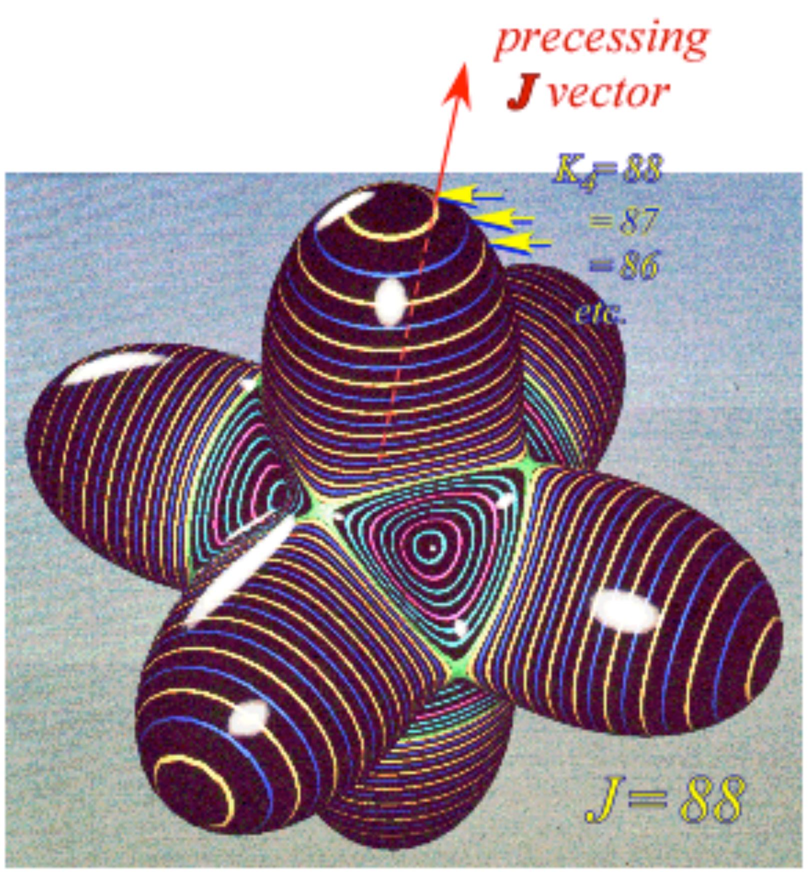
and J-cone intersection

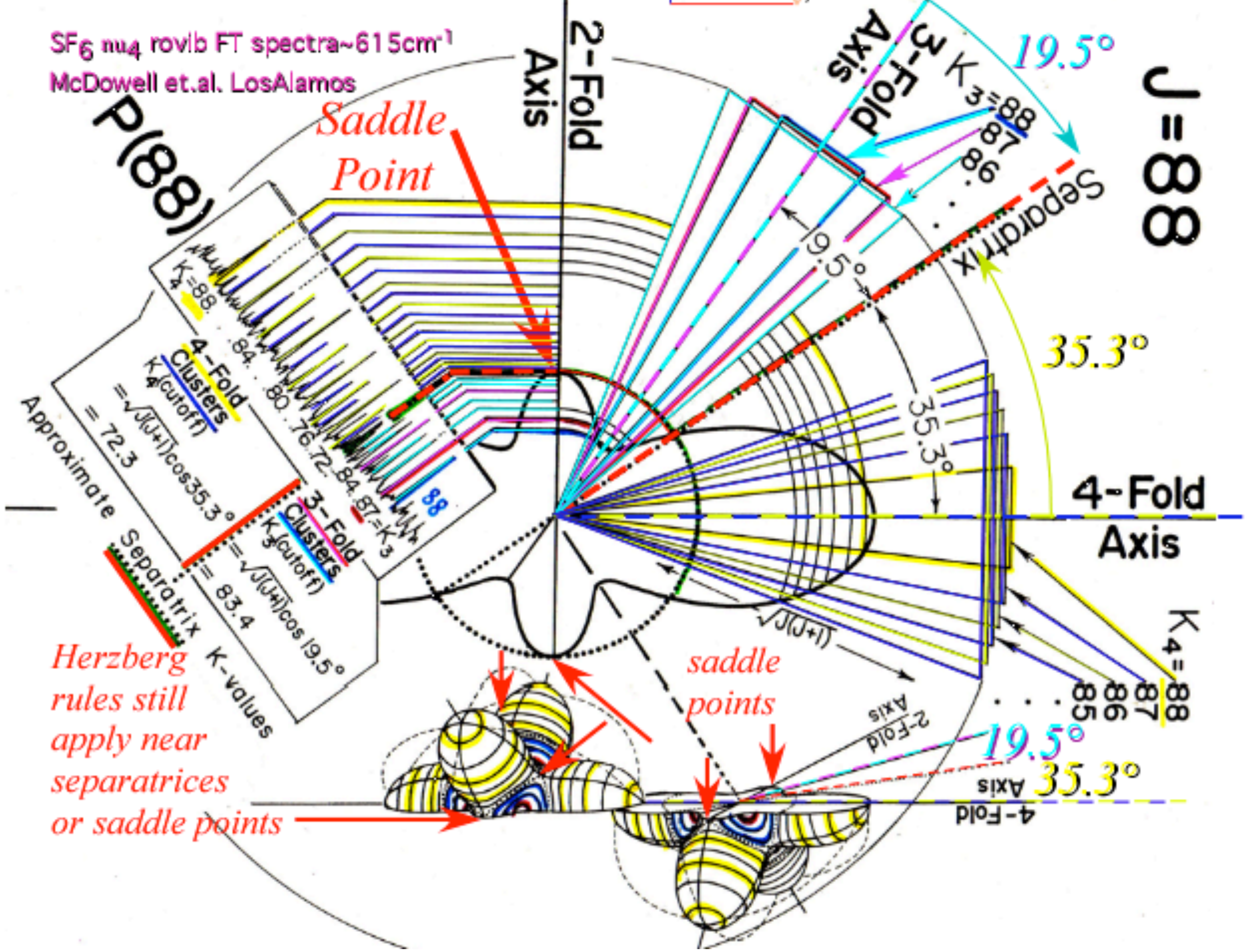
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

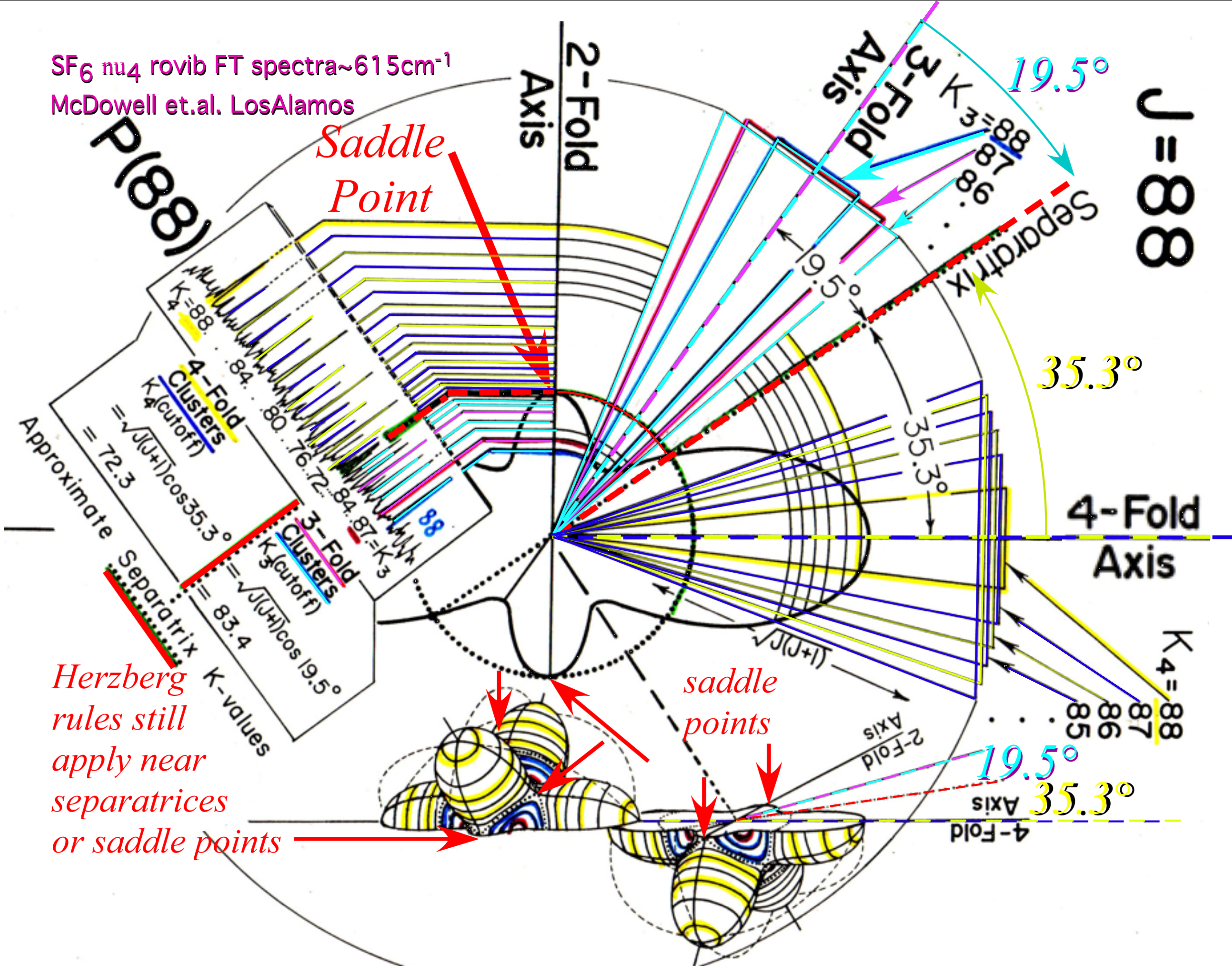
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



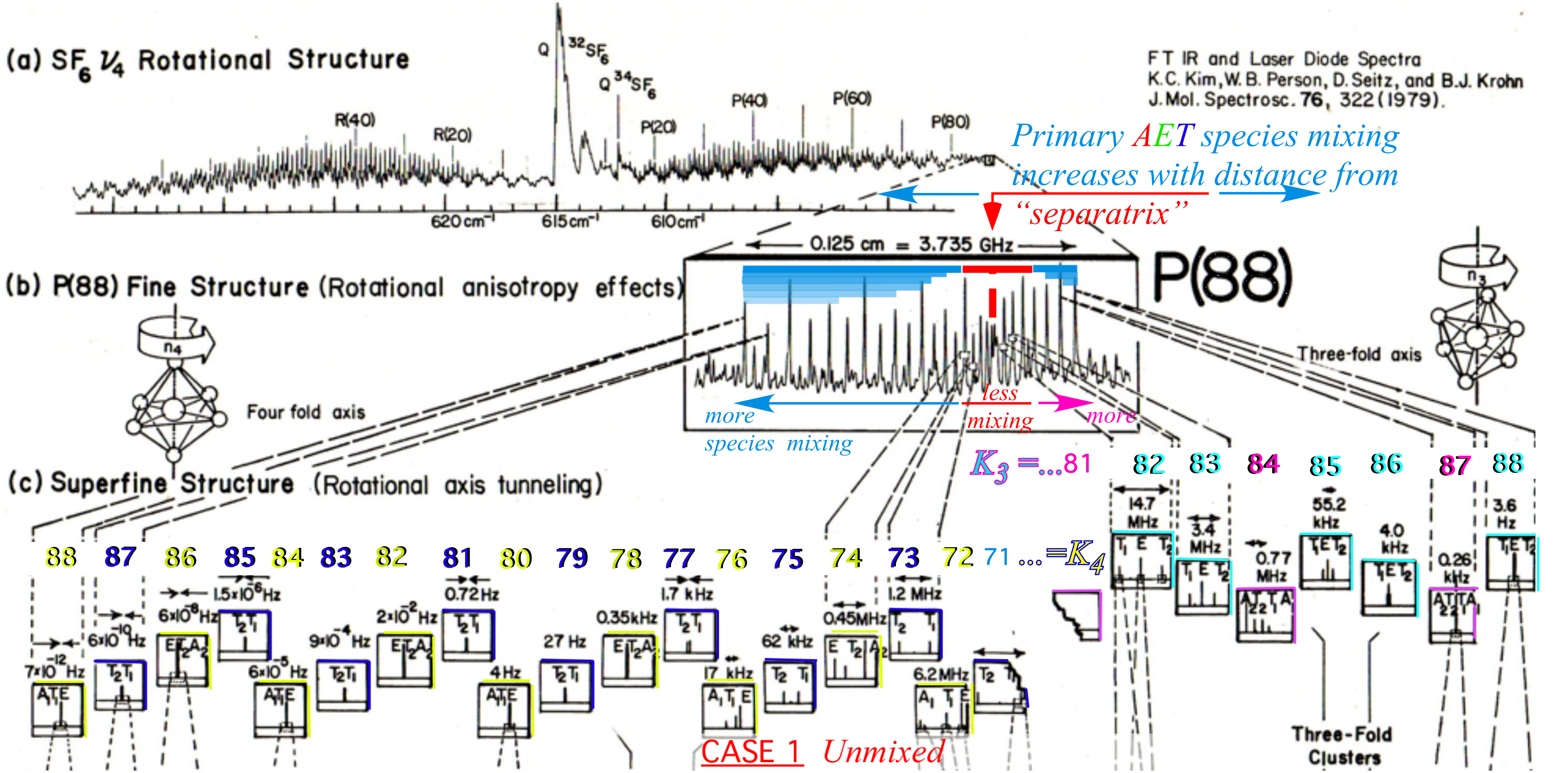
Rovibronic Energy (RE)
Tensor Surface







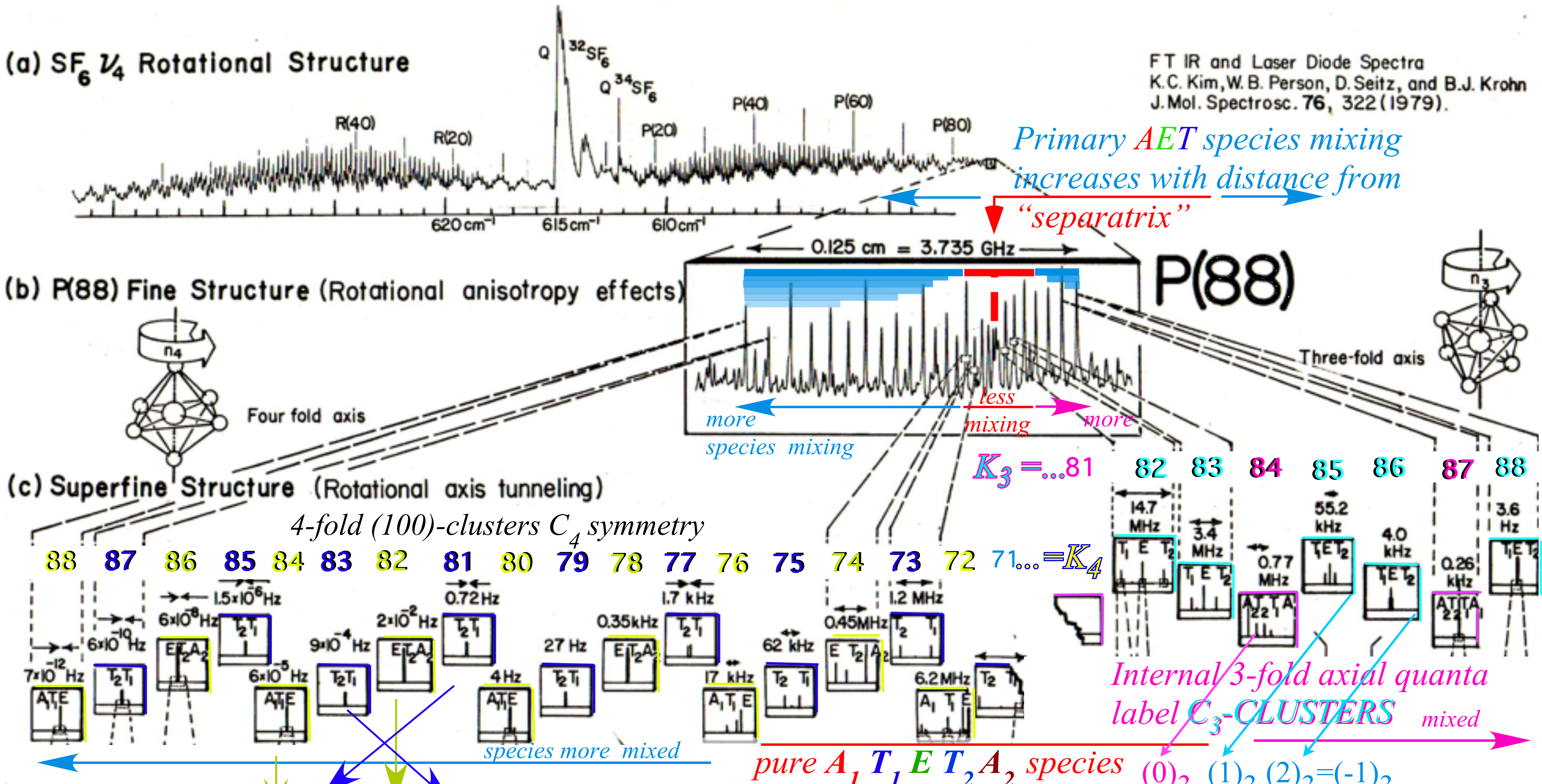
SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
Saddle Point
2-Fold Axis
3-Fold Axis
J=88
19.5°
Separatrix
35.3°
4-Fold Axis
4-Fold Clusters
3-Fold Clusters
Approximate Separatrix K-values
= 72.3
= 83.4
Herzberg rules still apply near separatrices or saddle points
saddle points
√J(J+1)



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)

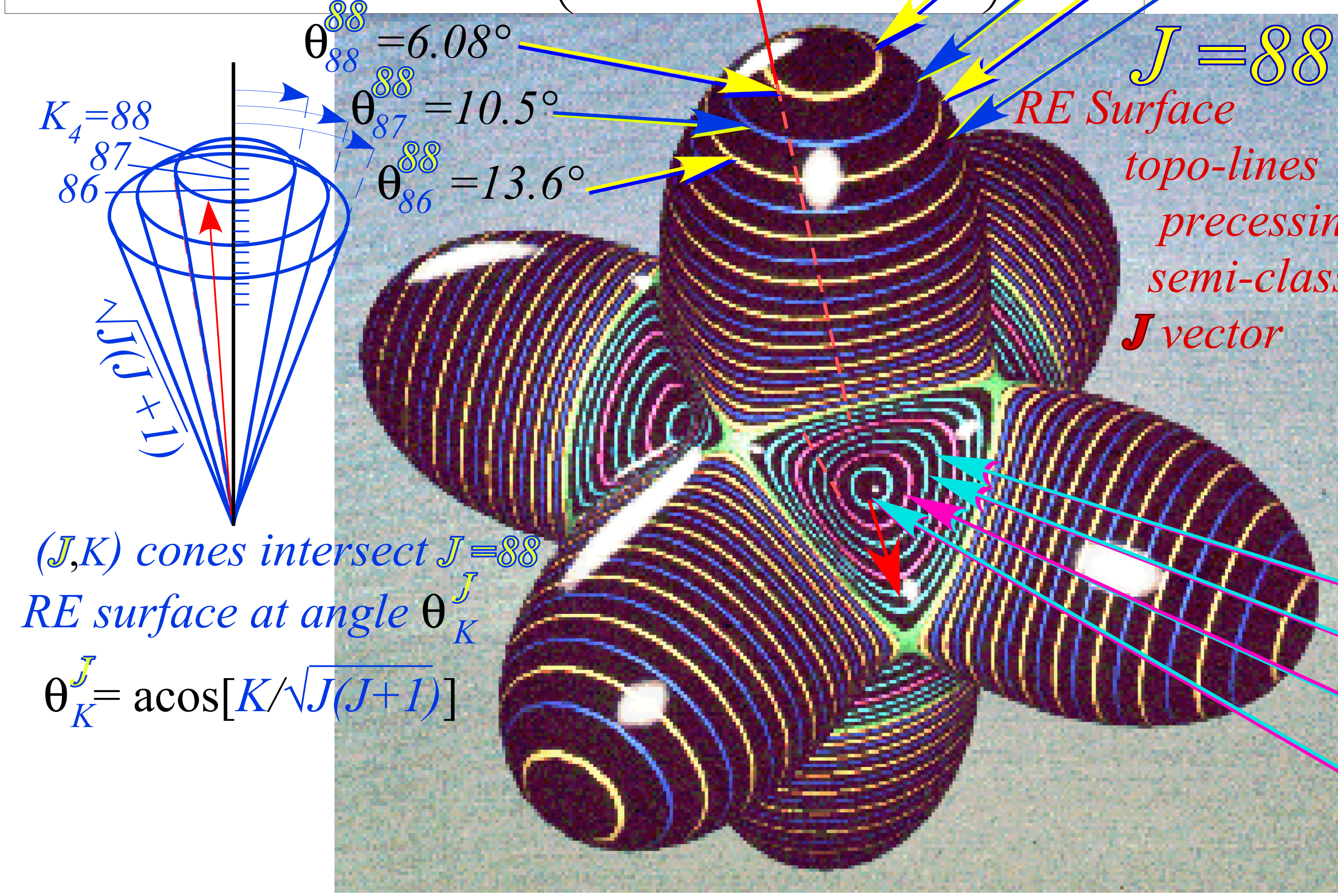
86=88-1

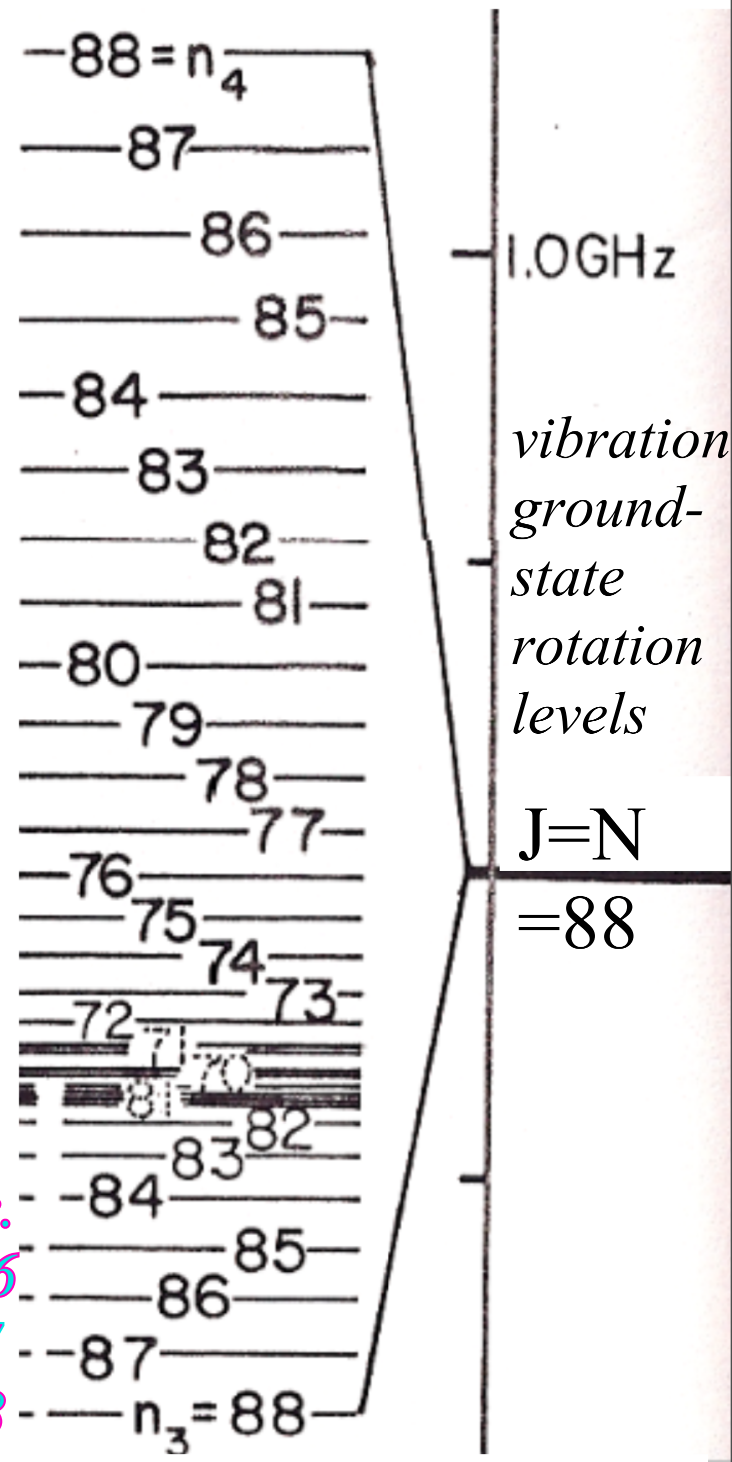
$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$

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

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

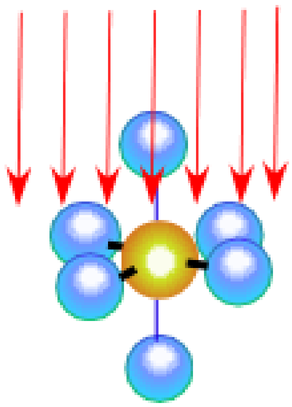
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$





Duality: The "Flip Side" of Symmetry Analysis.

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



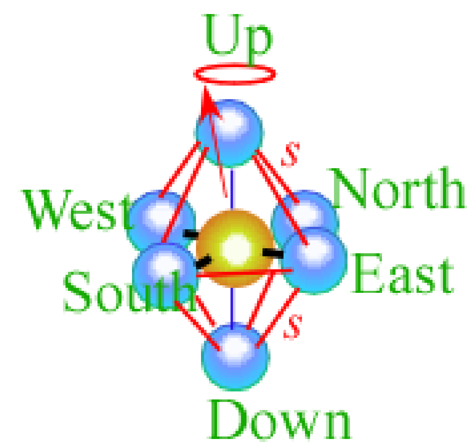
LAB versus BODY, *STATE versus PARTICLE,*
boils down to :
OUTSIDE versus INSIDE

Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

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

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

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



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

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

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LAB versus BODY, STATE versus PARTICLE,
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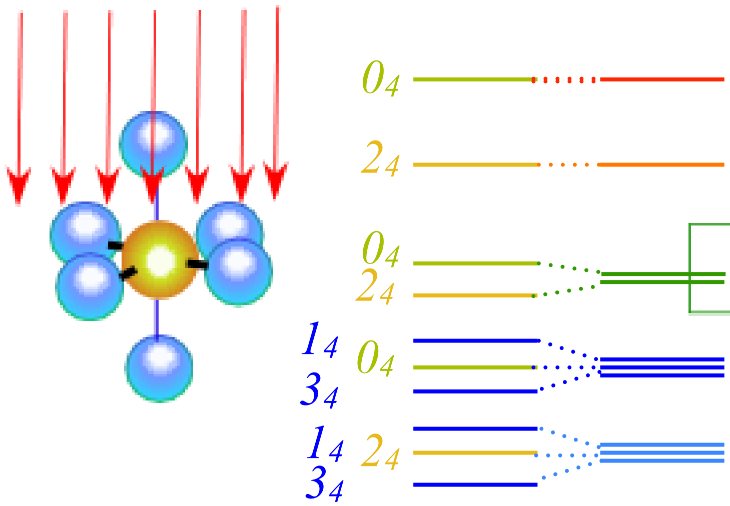
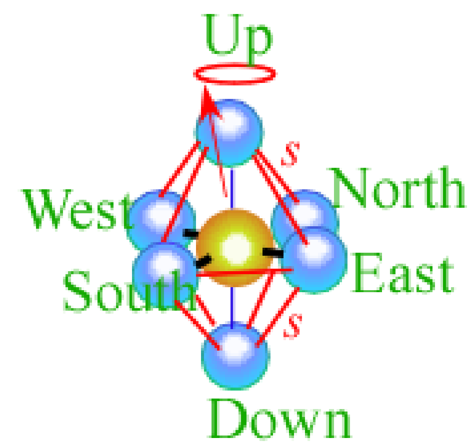


C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

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



|U>	|D>	|E>	|W>	|N>	|S>
H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H

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
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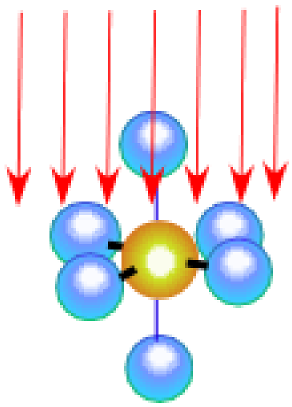
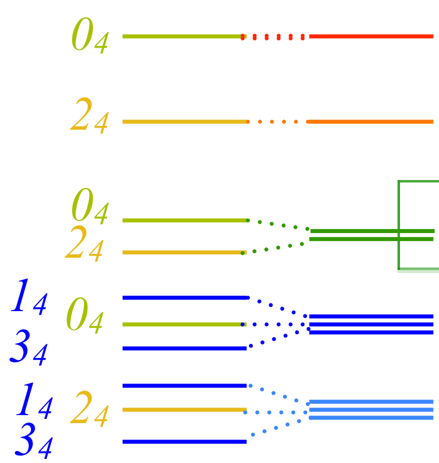
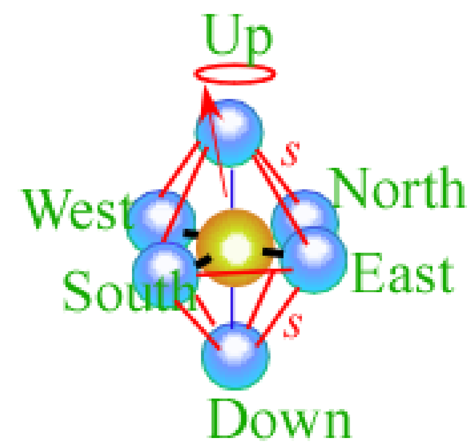
Example: Cubic-Octahedral O reduced to Tetragonal C_4





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

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

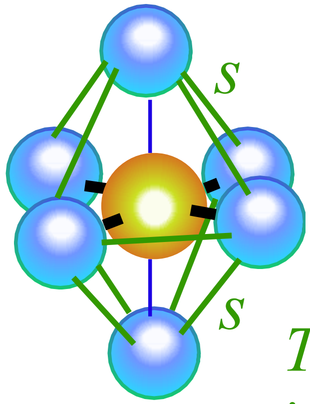


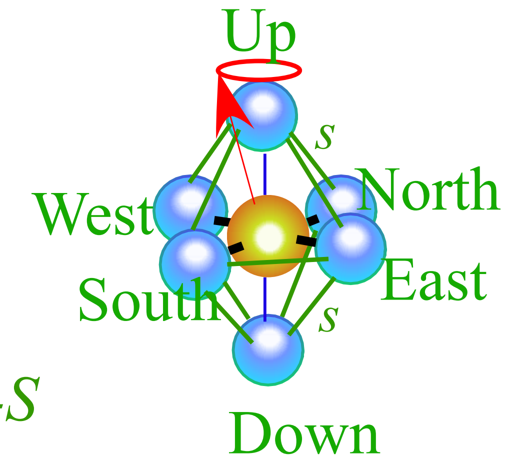
\|U>\|D>\|E>\|W>\|N>\|S>

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

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

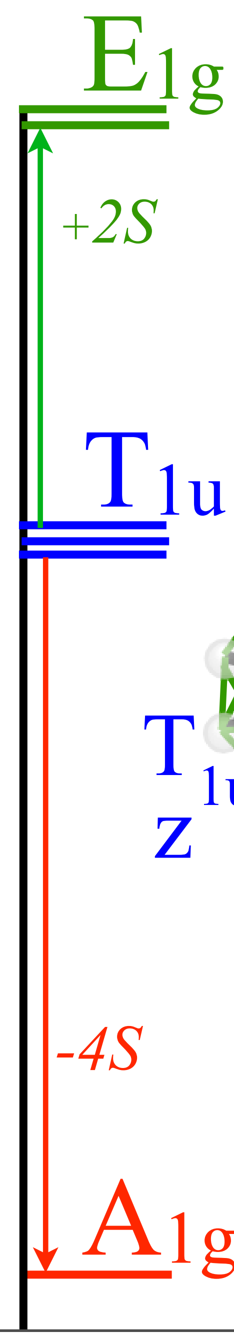
|U>|D>|E>|W>|N>|S>

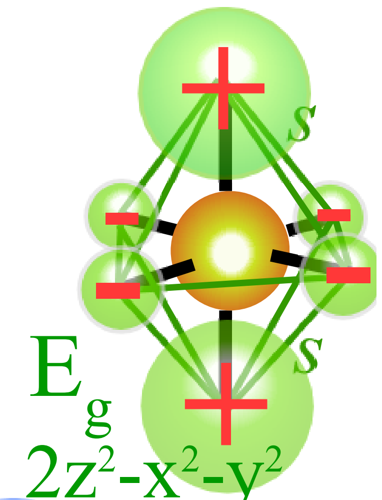
$$\begin{pmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{pmatrix}$$

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

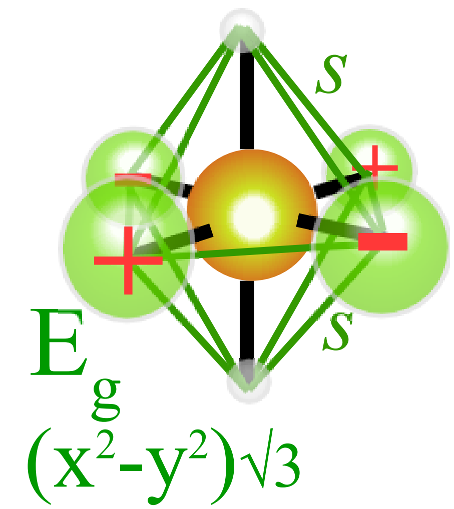
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}} = (H+0) \begin{vmatrix} +1 \\ -1 \\ 0 \\ 0 \\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

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

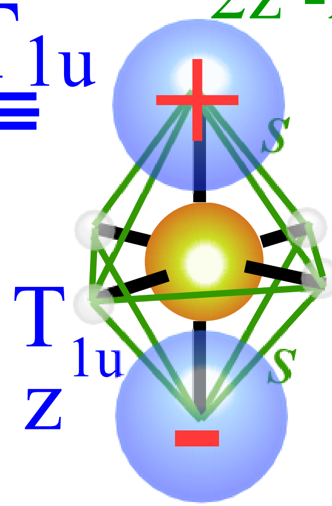




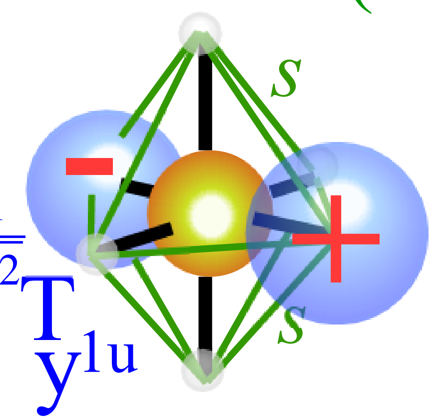
$$\begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$$

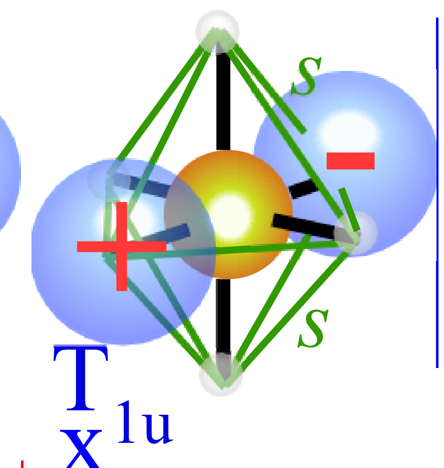


$$\begin{vmatrix} 0 \\ 0 \\ -1 \\ -1 \\ +1 \\ +1 \end{vmatrix} \frac{1}{2}$$

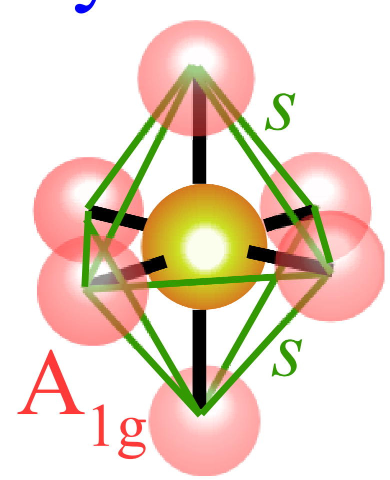


$$\begin{vmatrix} 0 \\ 0 \\ +1 \\ -1 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$$

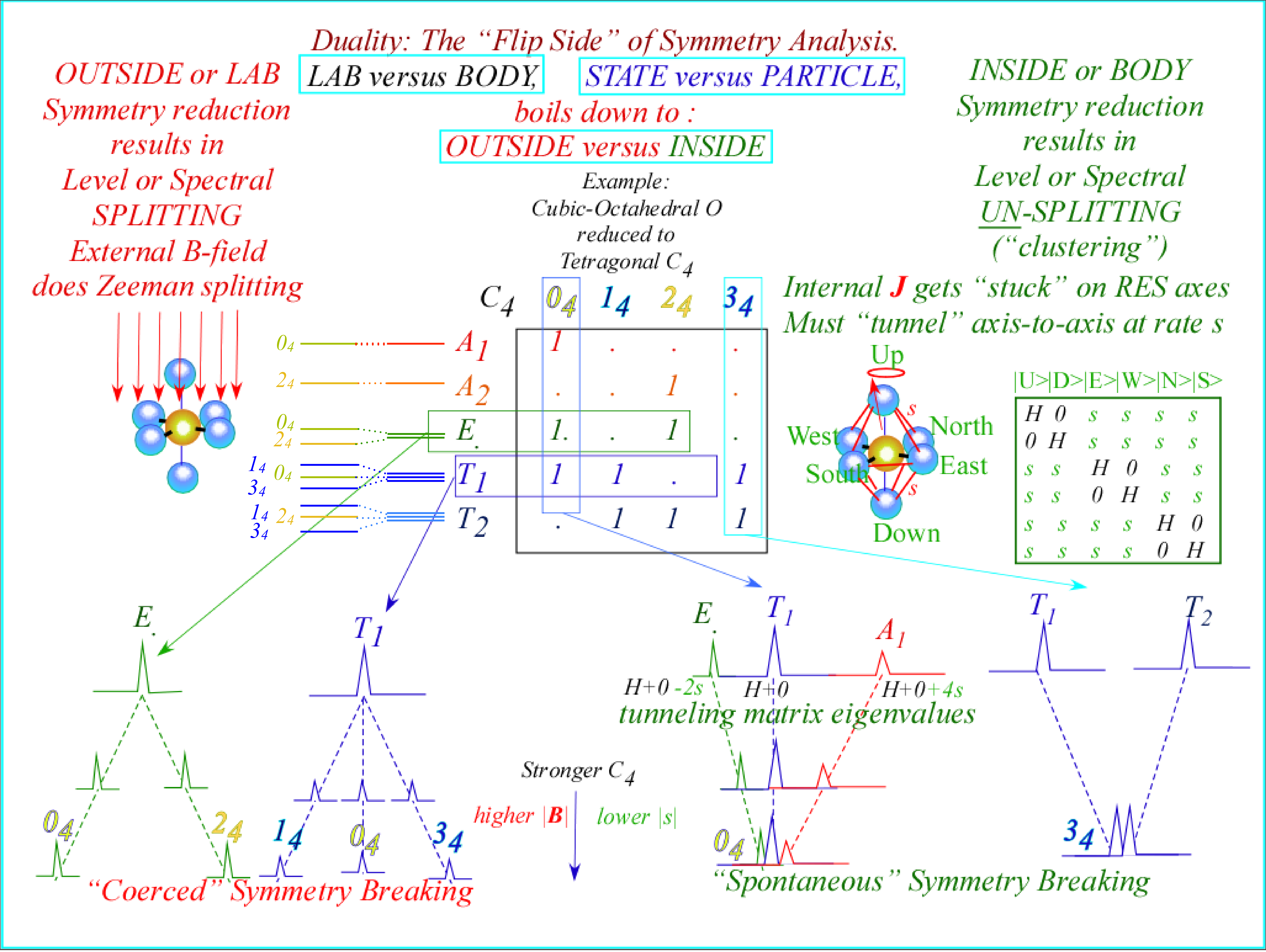




$$\begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ +1 \end{vmatrix} \frac{1}{\sqrt{2}}$$



$$\begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}}$$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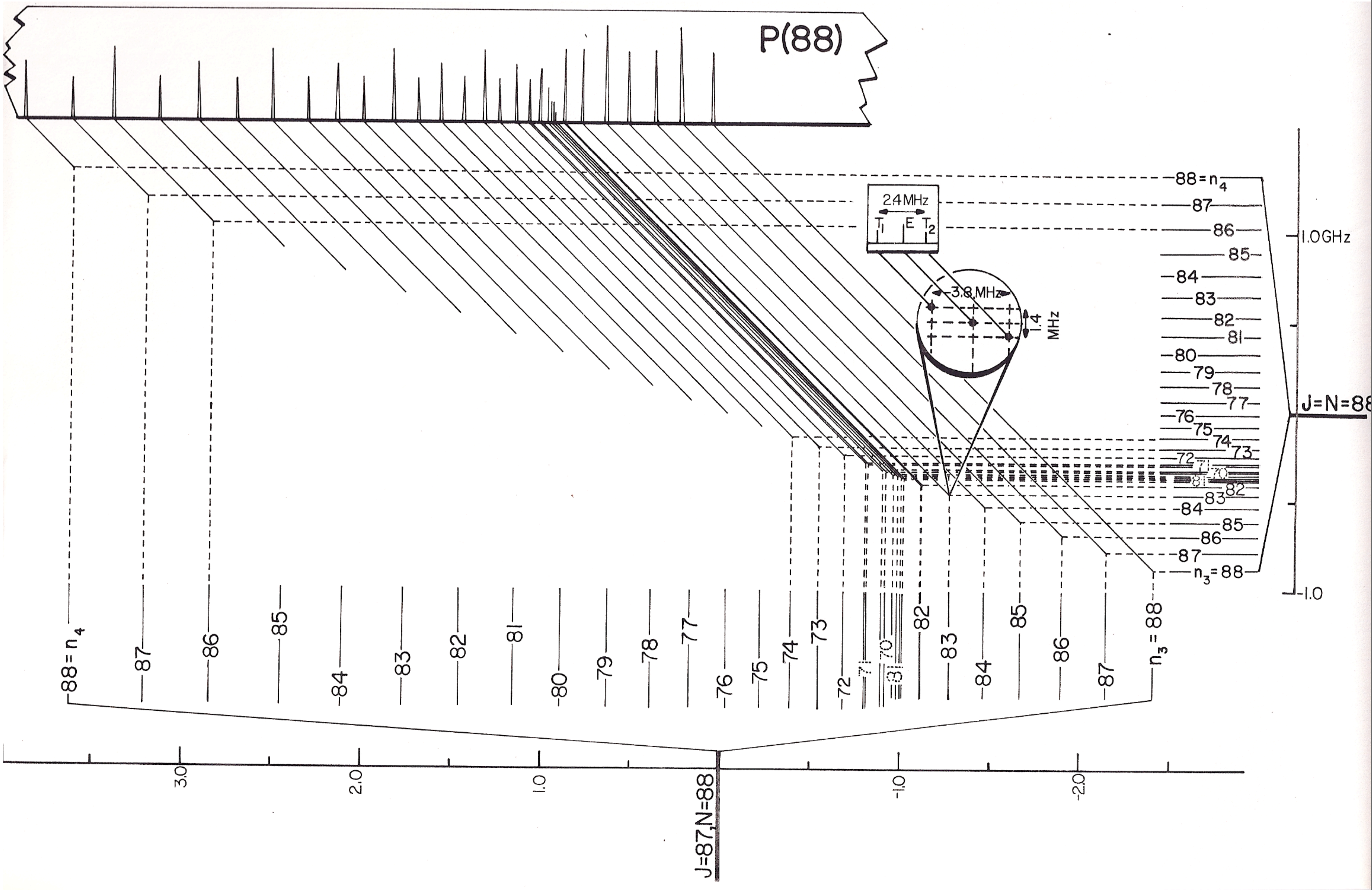
does Zeeman splitting
INSIDE or BODY
Symmetry reduction
results in
Level or Spectral
UN-SPLITTING
("clustering")
Example:
Cubic-Octahedral O
reduced to
Tetragonal C4
C4 04 14 24 34
A1 1 . . .
A2 . . 1 .
E 1. . 1 .
T1 1 1 . 1
T2 . 1 1 1
Internal J gets "stuck" on RES axes
Must "tunnel" axis-to-axis at rate s
Up
West
North
South
East
Down
|U>|D>|E>|W>|N>|S>
H 0 s s s s
0 H s s s s
s s H 0 s s
s s 0 H s s
s s s s H 0
s s s s 0 H
E
T1
A1
H+0 -2s
H+0
H+0+4s
tunneling matrix eigenvalues
T1
T2
E
T1
04
24
14
04
34
Stronger C4
higher |B|
lower |s|
04
34
"Coerced" Symmetry Breaking
"Spontaneous" Symmetry Breaking


P(88)
2.4MHz
T1 E T2
3.8 MHz
1.4 MHz
1.0GHz
-1.0
J=N=88
88=n4
n3=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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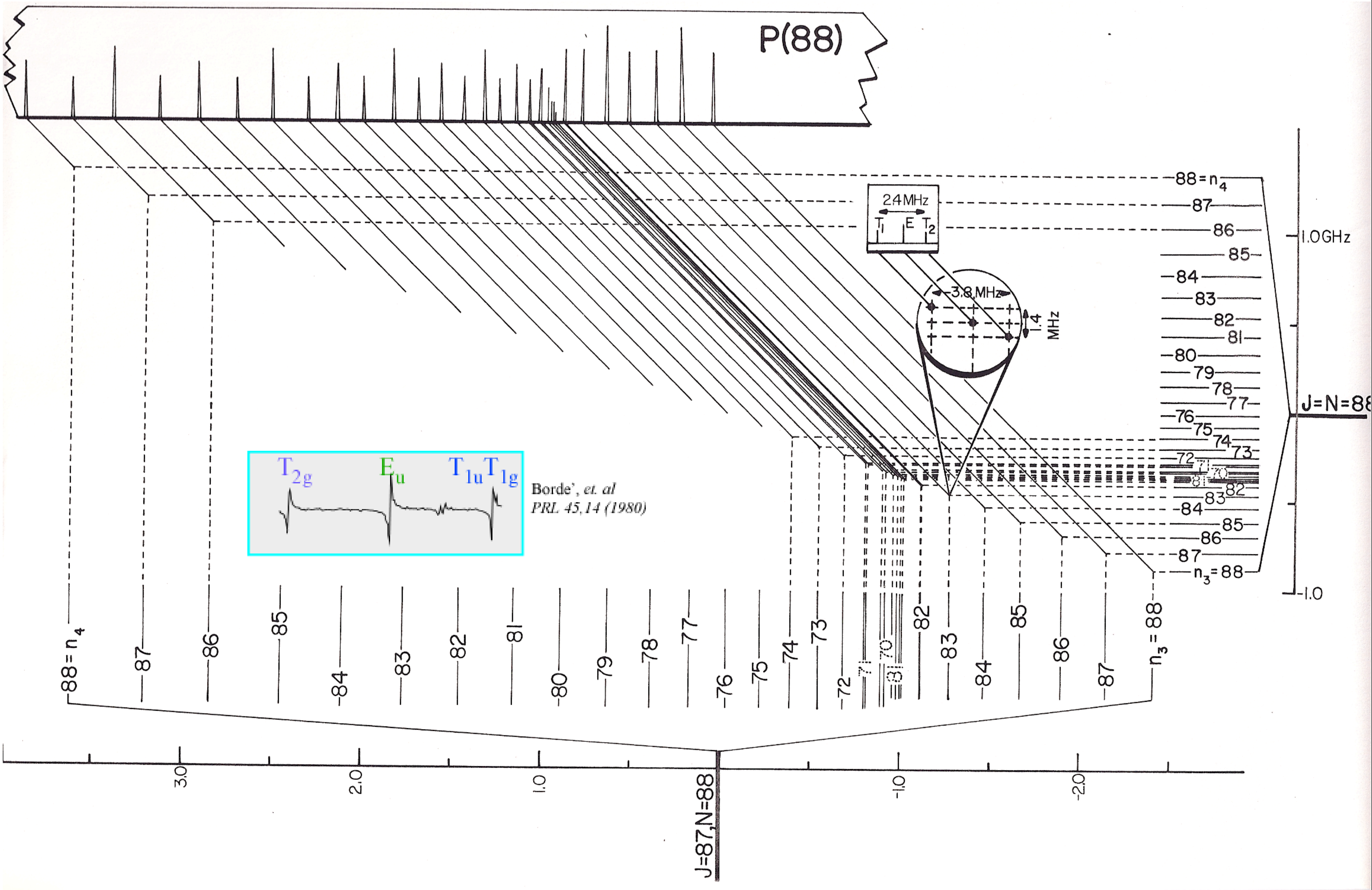
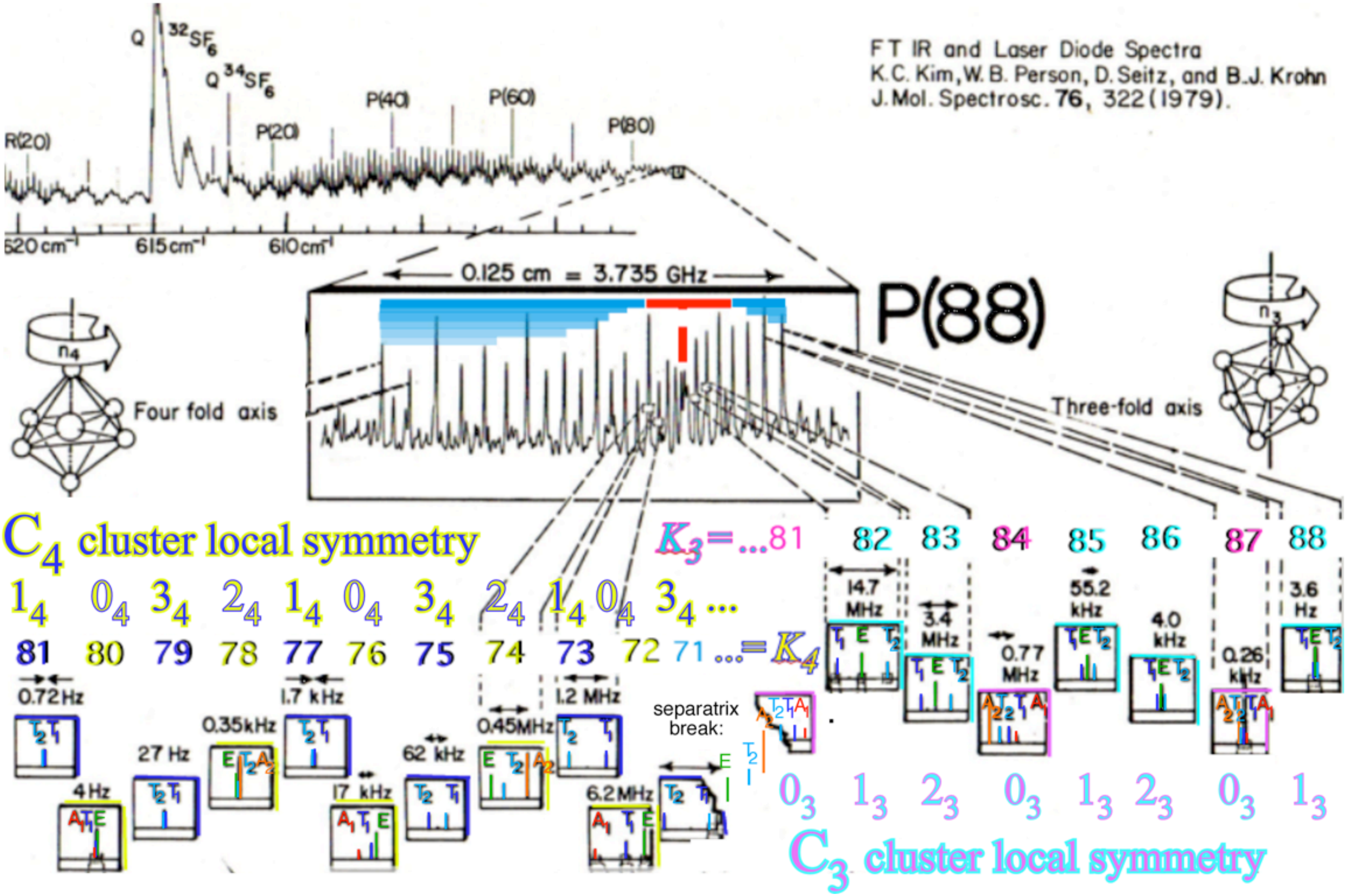
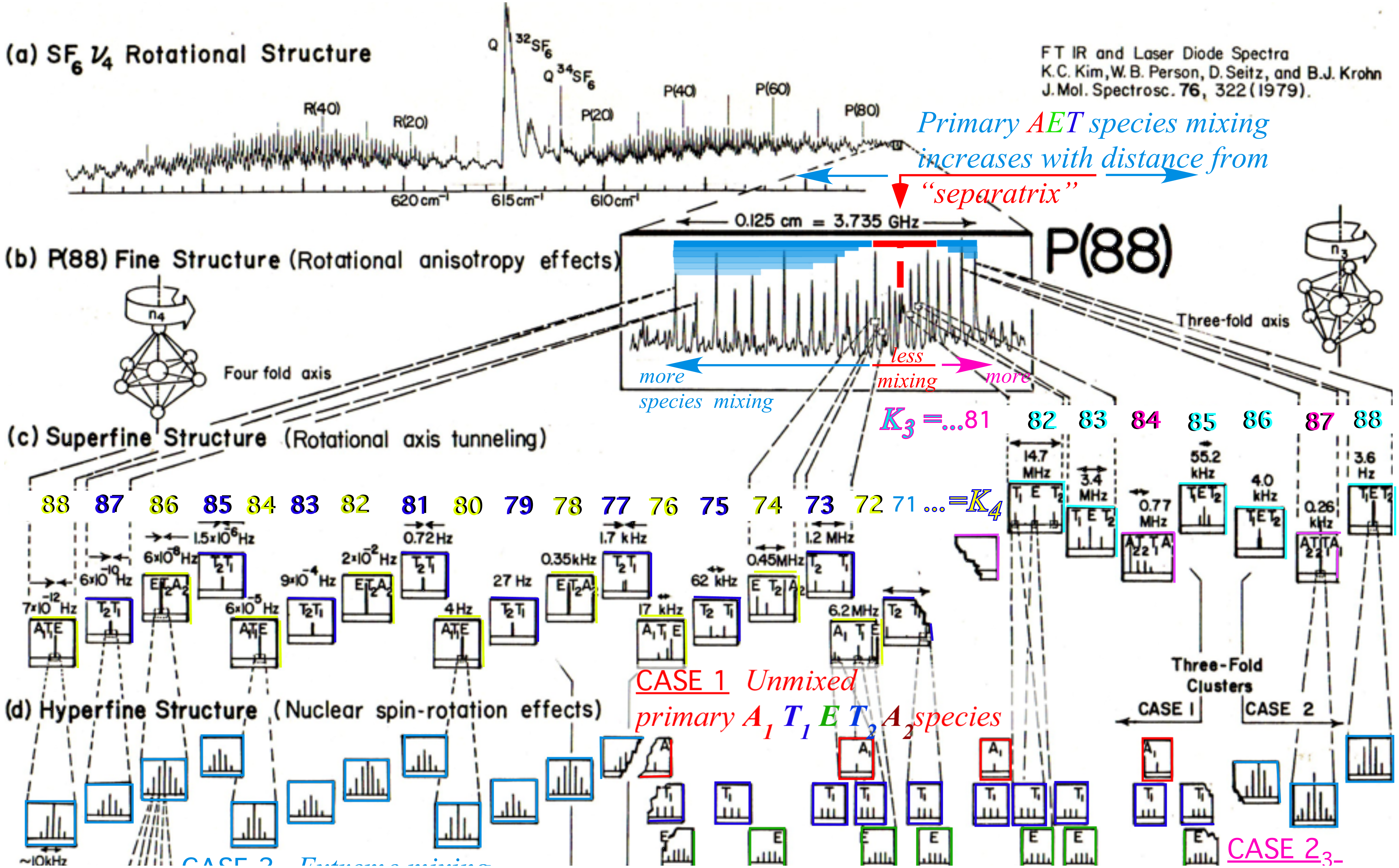


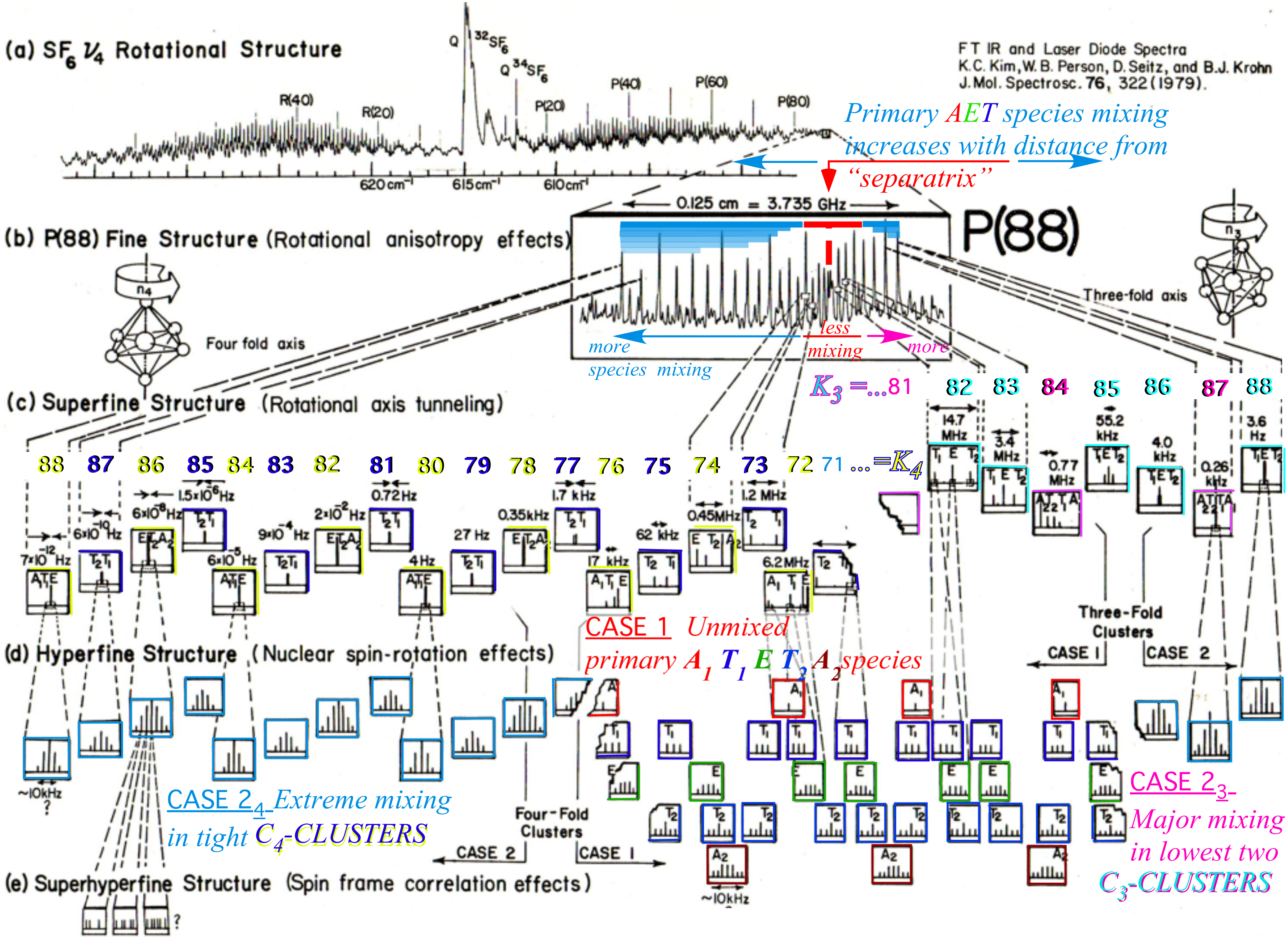
P(88)
2.4 MHz
T_1 E T_2
3.8 MHz
1.4 MHz
1.0 GHz
-1.0
J=N=88
88=n_4
n_3=88
J=87, N=88
3.0
2.0
1.0
-1.0
-2.0
T_{2g} E_u T_{1u} T_{1g}
Borde', et. al
PRL 45,14 (1980)

IR Spectra of SF6 ν₄ P(88)



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


(a) SF6 ν4 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)
0.125 cm = 3.735 GHz
P(88)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 =...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 ...=K4
(d) Hyperfine Structure (Nuclear spin-rotation effects)
CASE 1 Unmixed primary A1 T1 E T2 A2 species
Three-Fold Clusters
CASE 1
CASE 2
CASE 23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Q 32SF6
Q 34SF6
R(40)
R(20)
P(20)
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P(80)
620 cm-1
615 cm-1
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(d) Hyperfine Structure (Nuclear spin-rotation effects)
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CASE 1
CASE 2
Four-Fold Clusters
CASE 2
CASE 1
CASE 24 Extreme mixing in tight C4-CLUSTERS
CASE 23 Major mixing in lowest two C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
~10kHz

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

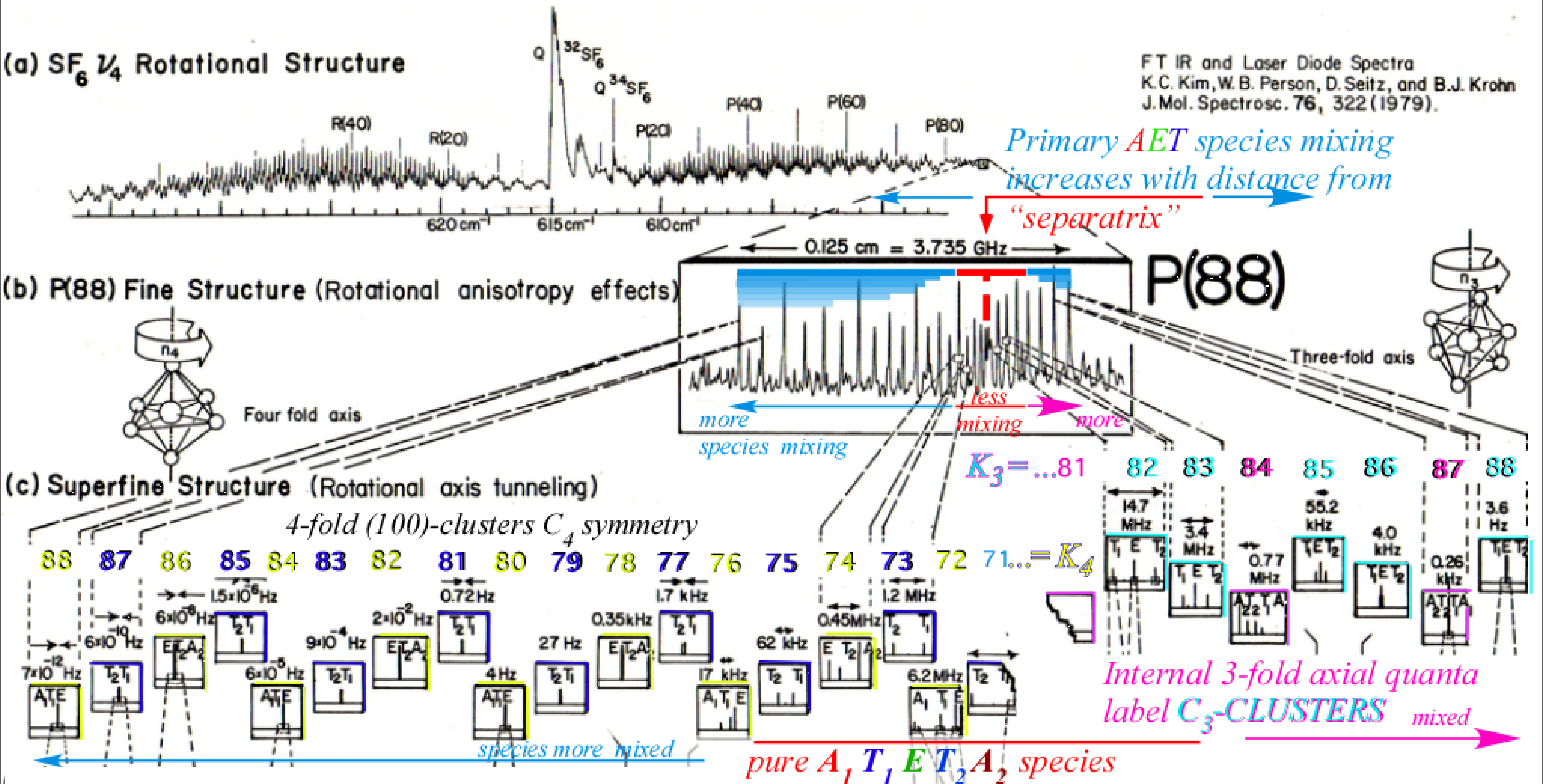
OUTLINE

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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P(88)
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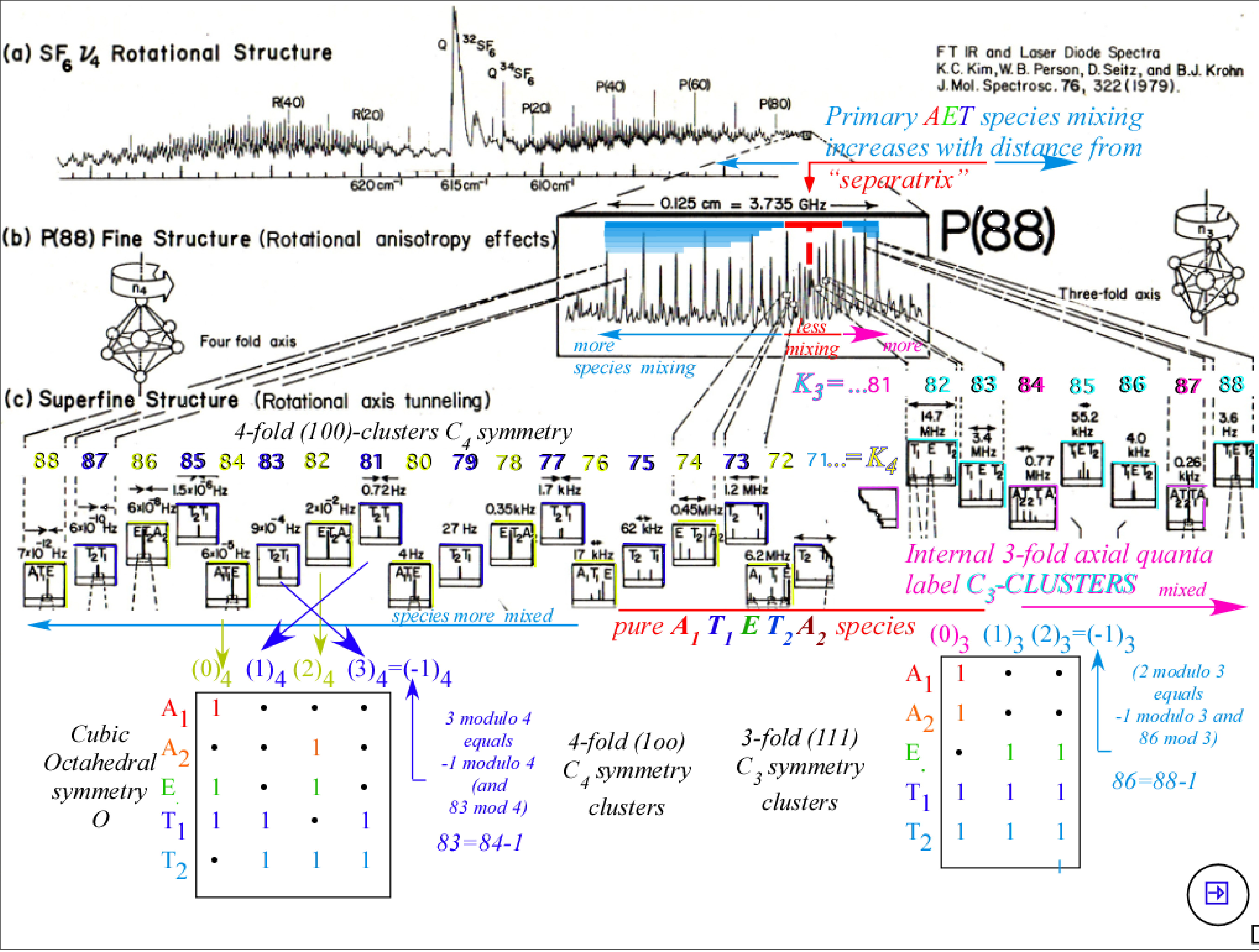
Four fold axis
Three-fold axis
more
species mixing
less
mixing
more
(c) Superfine Structure (Rotational axis tunneling)
4-fold (100)-clusters C4 symmetry
K3= ...81
82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71...=K4
Internal 3-fold axial quanta
label C3-CLUSTERS
mixed
species more mixed
pure A1 T1 E T2 A2 species



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

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

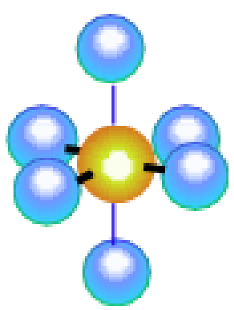
Entanglement!

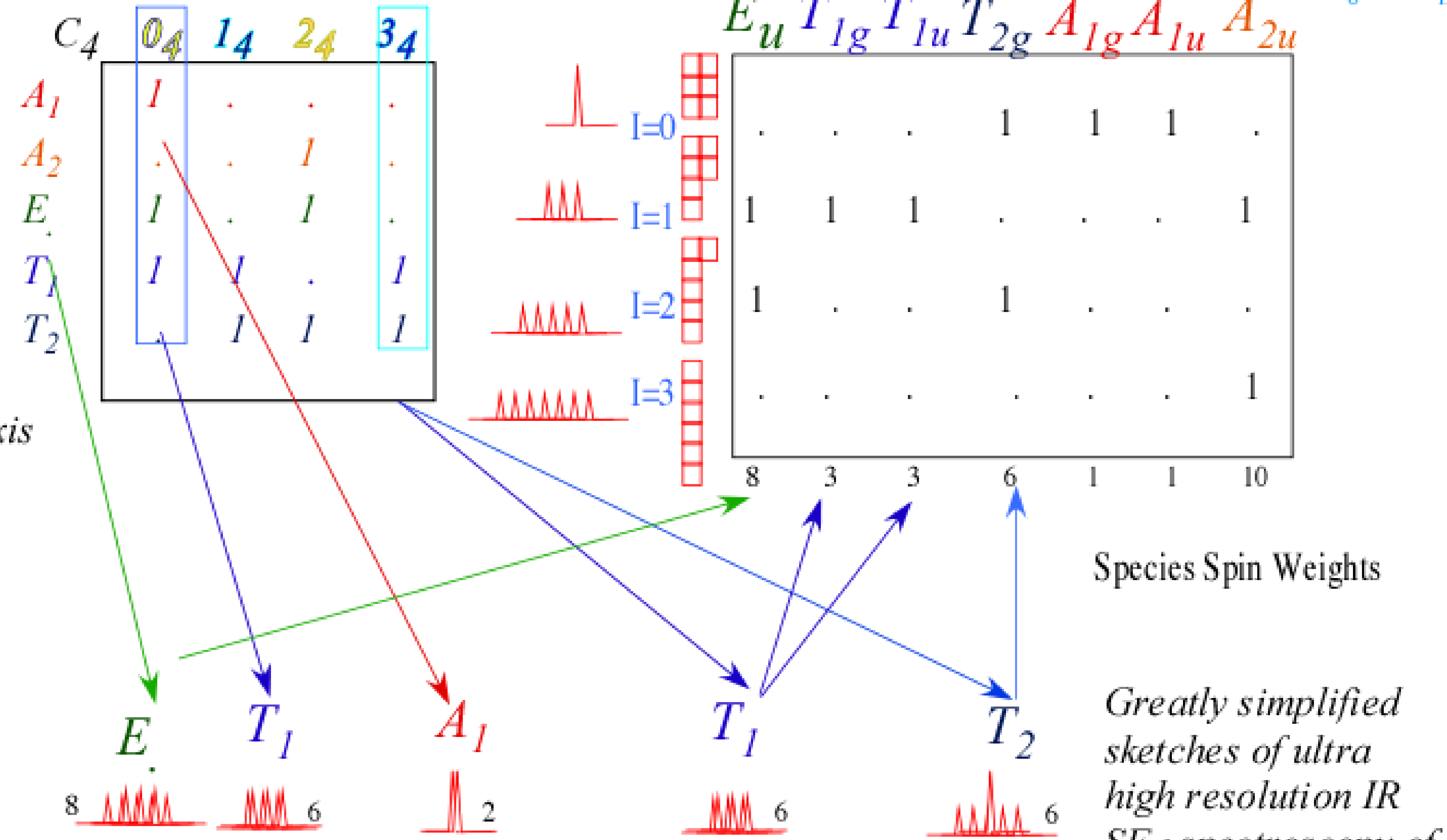
How F-nuclei become distinguished

(but not distinguish<u>able</u>)

in SF_6.

If rotation is not too stuck on C_4 axis all six nuclei are equivalent





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

	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
	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 who did SiF_4, too.

DISentanglement!

How F-nuclei become distinguished

(but not distinguishable)

in SF_6.

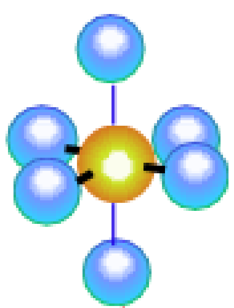
C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

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

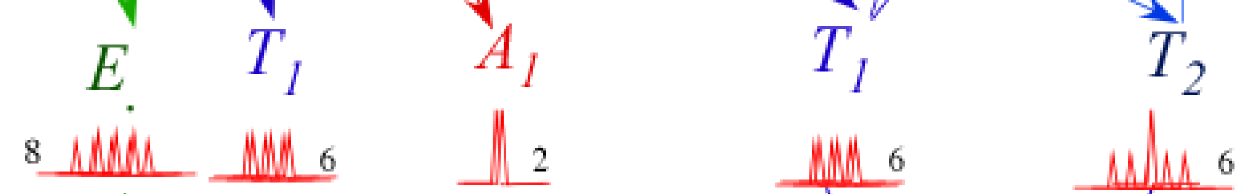
	E_u	T_{1g}	T_{1u}	T_{2g}	A_{1g}	A_{1u}	A_{2u}
I=0	.	.	.	1	1	1	.
I=1	1	1	1	.	.	.	1
I=2	1	.	.	1	.	.	.
I=3	.	.	.	.	.	.	1
	8	3	3	6	1	1	10

Species Spin Weights

If rotation is not too 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"



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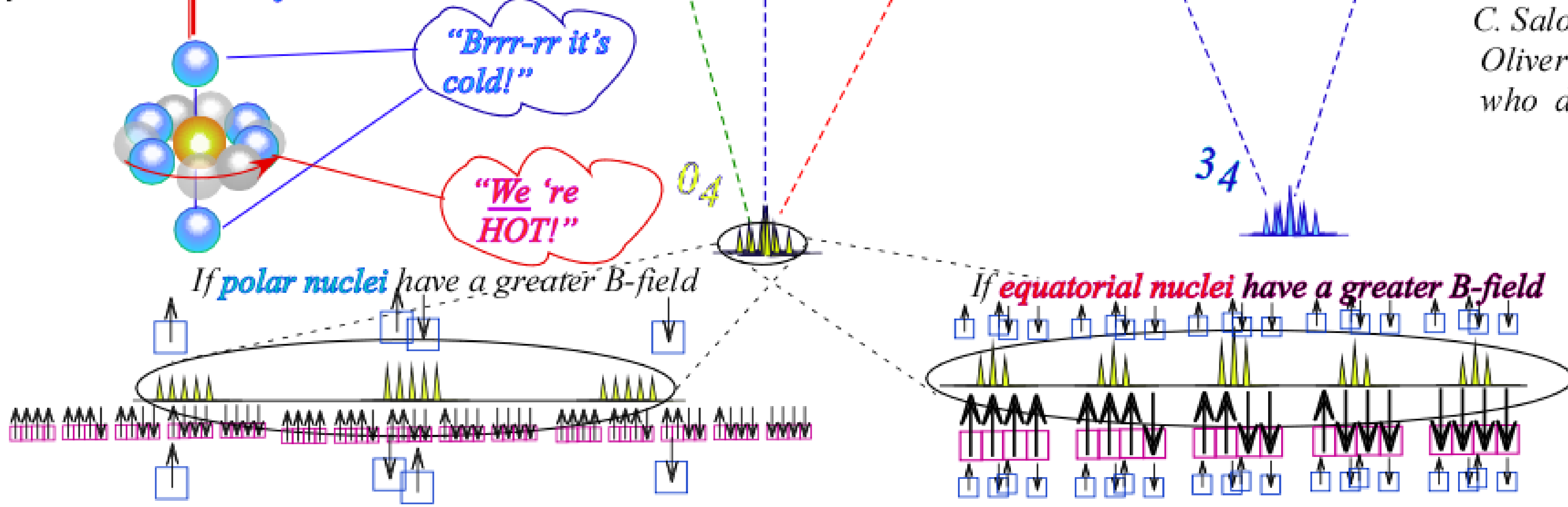

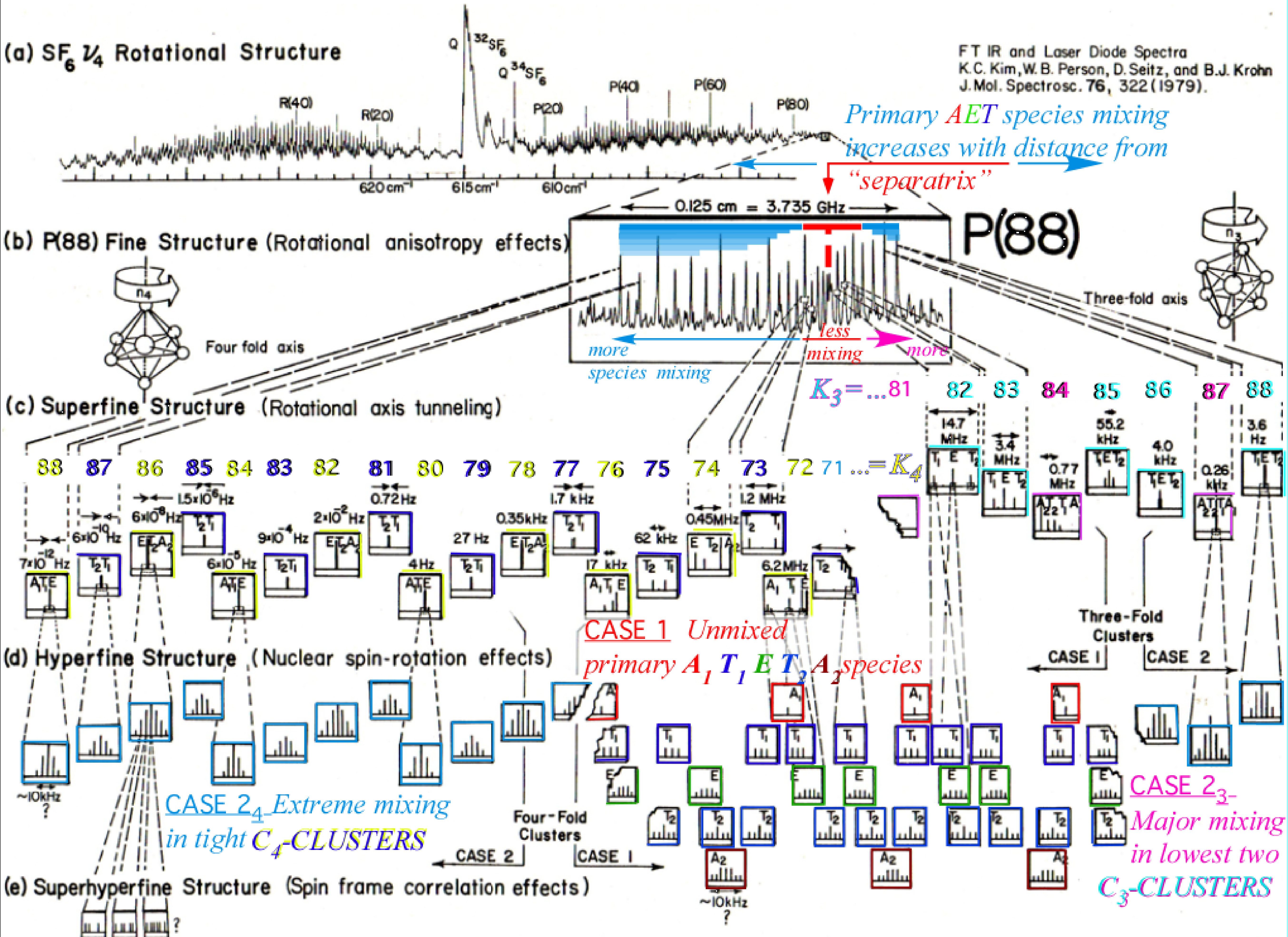
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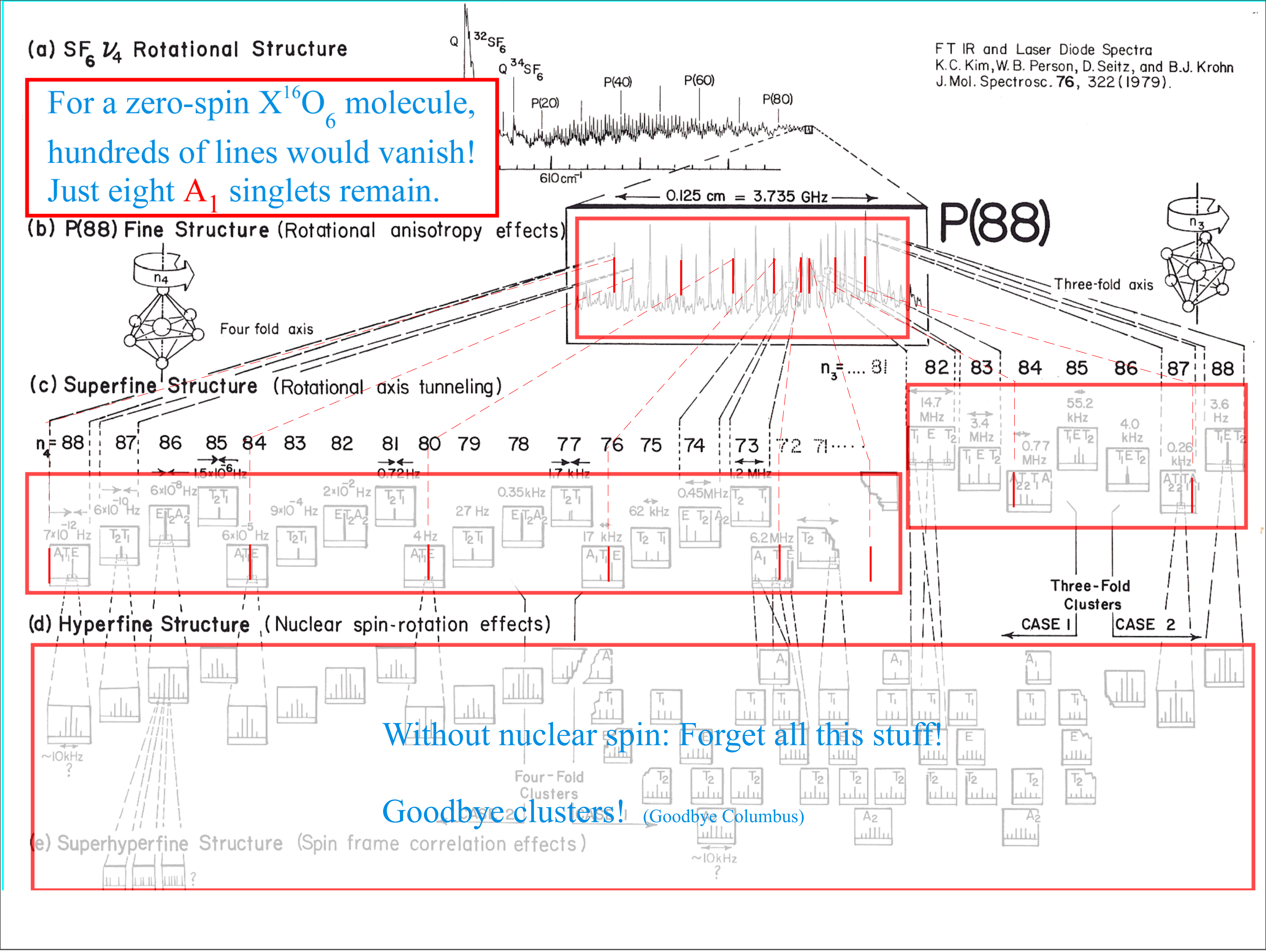
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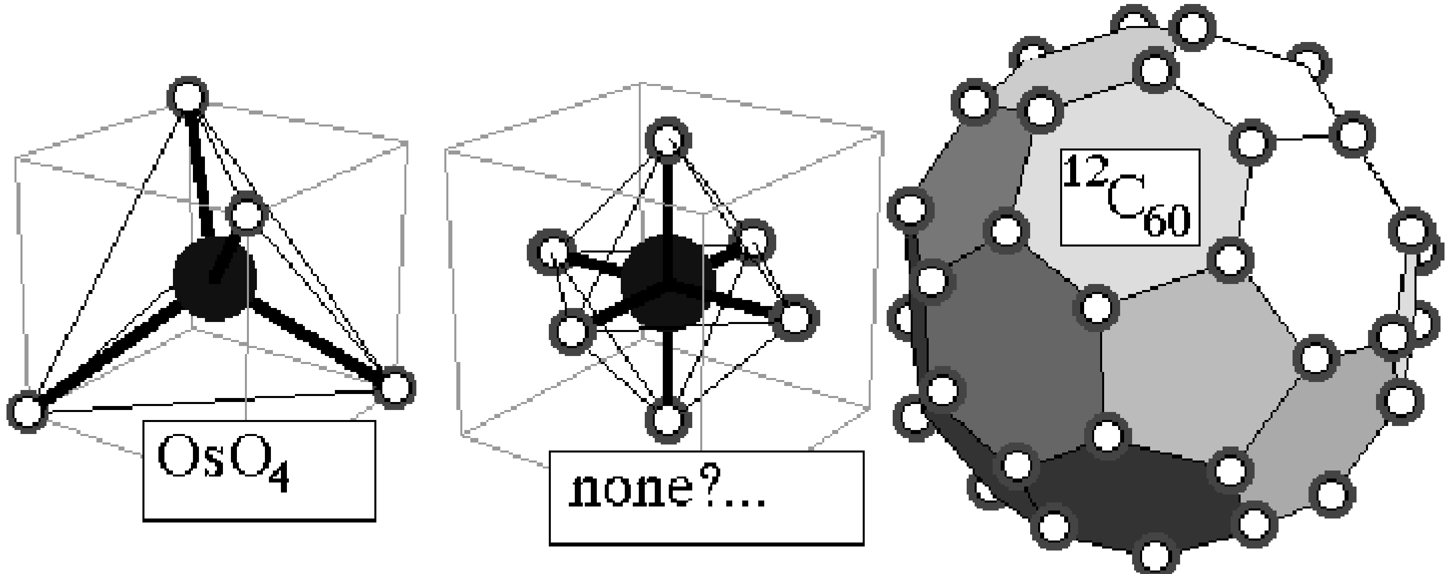
J. Mol. Spectrosc. 76, 322 (1979).
For a zero-spin X16O6 molecule, hundreds of lines would vanish!
Just eight A1 singlets remain.
Q 32SF6
Q 34SF6
P(20)
P(40)
P(60)
P(80)
610 cm-1
0.125 cm = 3.735 GHz
P(88)
(b) P(88) Fine Structure (Rotational anisotropy effects)
Four fold axis
Three-fold axis
(c) Superfine Structure (Rotational axis tunneling)
n4 = 88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71....
n3 = ... 81 82 83 84 85 86 87 88
Three-Fold Clusters
CASE 1
CASE 2
(d) Hyperfine Structure (Nuclear spin-rotation effects)
Without nuclear spin: Forget all this stuff!
Four-Fold Clusters
Goodbye clusters! (Goodbye Columbus)
(e) Superhyperfine Structure (Spin frame correlation effects)

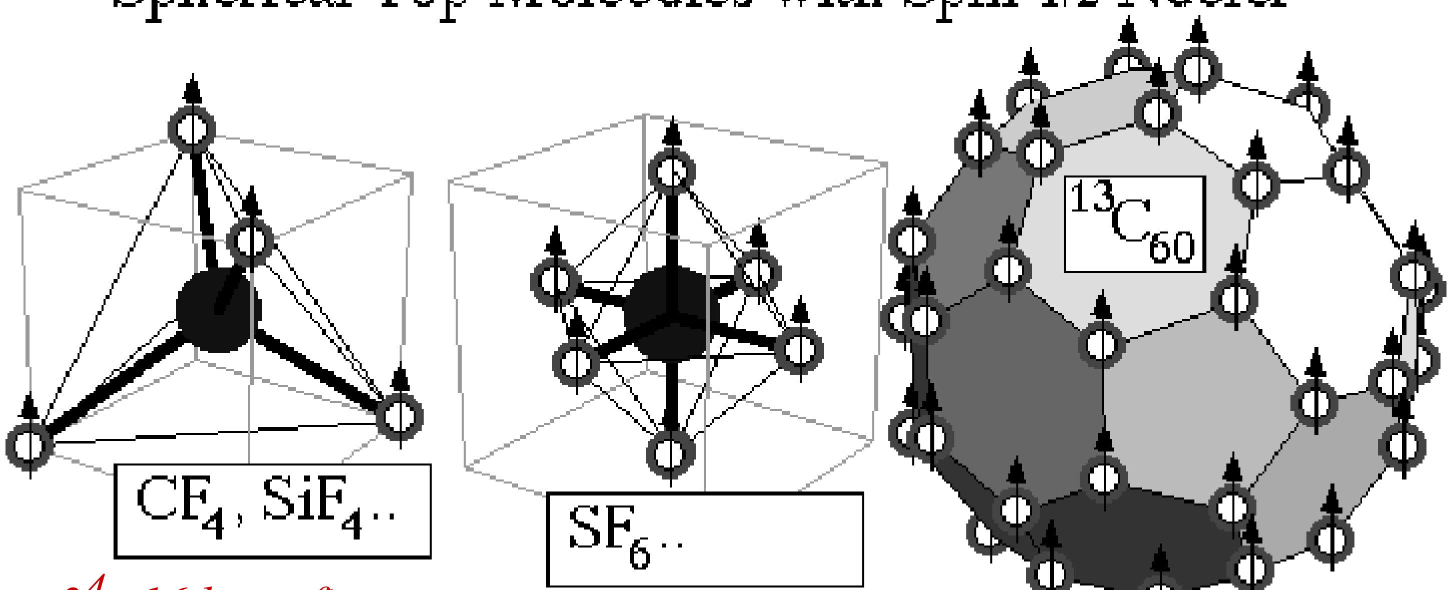
Some examples of Bose Exclusion

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

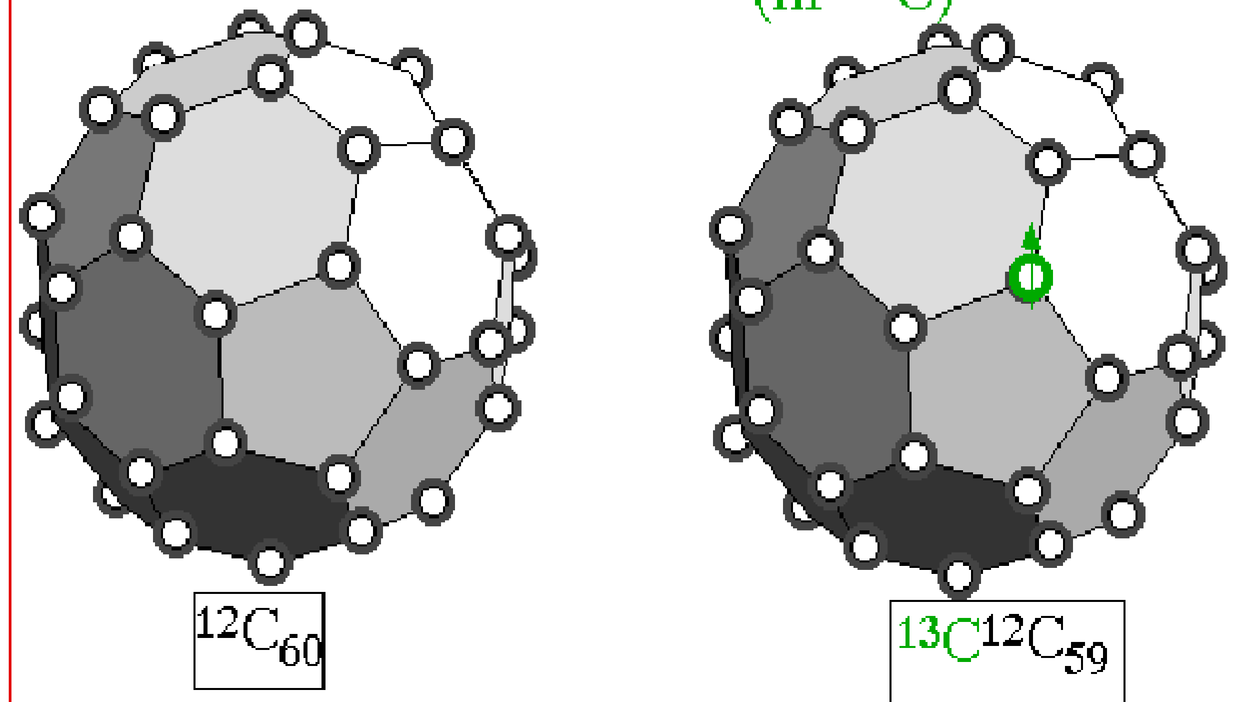
2^6=64 hyperfine states: I=0-3

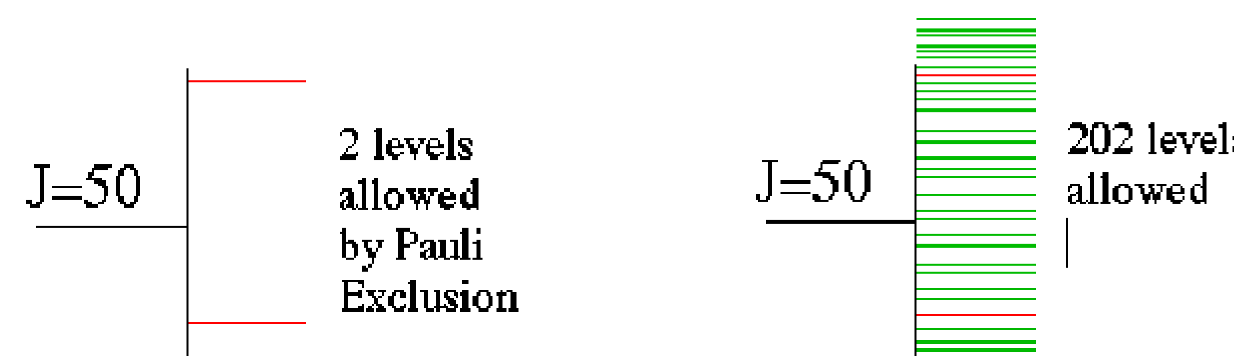
2^{60}=1.15x10^{18} hyperfine states: I=0-30

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:*

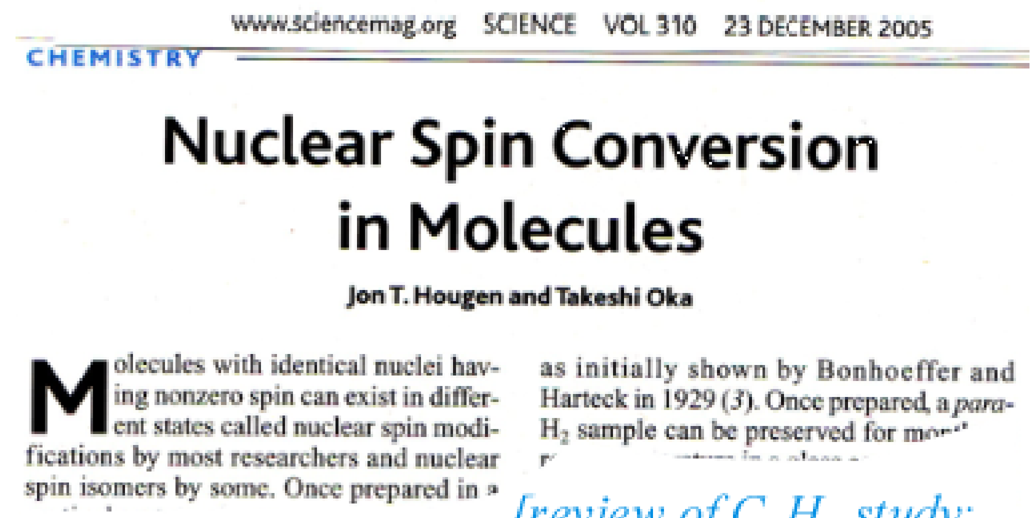
Old *(1939, 1945, and 1966)* — *versus* — *New (1978- present)*

"...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... " "



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?

Widespread and extreme mixing of species (perversion) *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}

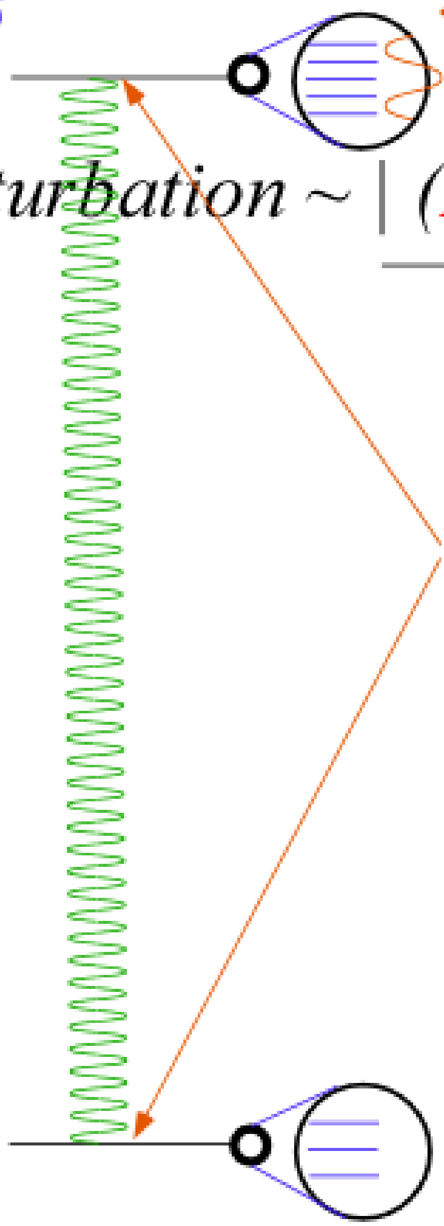
No Way!

...because nuclear moments...

...are so very slight..."

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

E_{2g}^{5}



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

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

A_{1g}^{3}

HOW CONSERVED (or perverted?) IS ROVIBRONIC-SPIN SYMMETRY?

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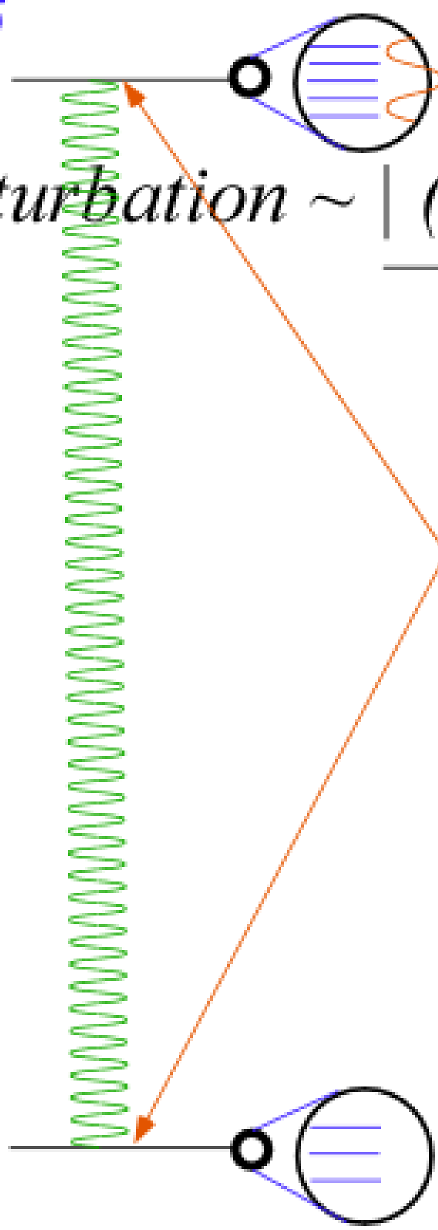
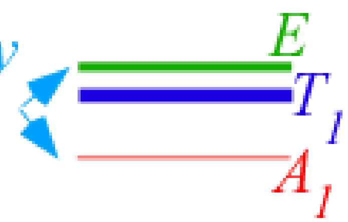


...too darn small (~kHz)...

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

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

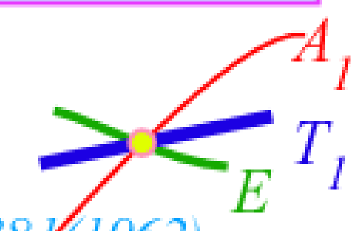
...exponentially tiny!
(like 10^{-50}Hz)



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

WAY!

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



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

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

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

RE Superhyperfine transitions
Hyperfine effects may rule! A_1 T_1 E T_2 A_2 get seriously mixed up.
Harter, Patterson, and daPaixao, Rev.Mod.Phys. 50, 37(1978)
Harter and Patterson, Phys. Rev. A19,2277(1979) (CF_4)
Harter, Phys. Rev. A24,192-262(1981) (SF_6)

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- *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

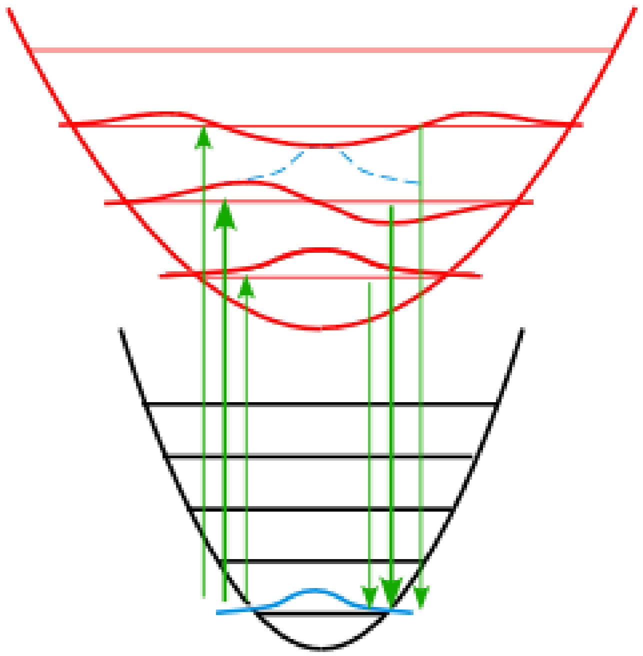
- *Analogy between PE surface and RES dynamics*
- *Rotational Energy Eigenvalue Surfaces (REES)* — ν_3 SF_6

Potenial Energy Surface (PES) Dynamics

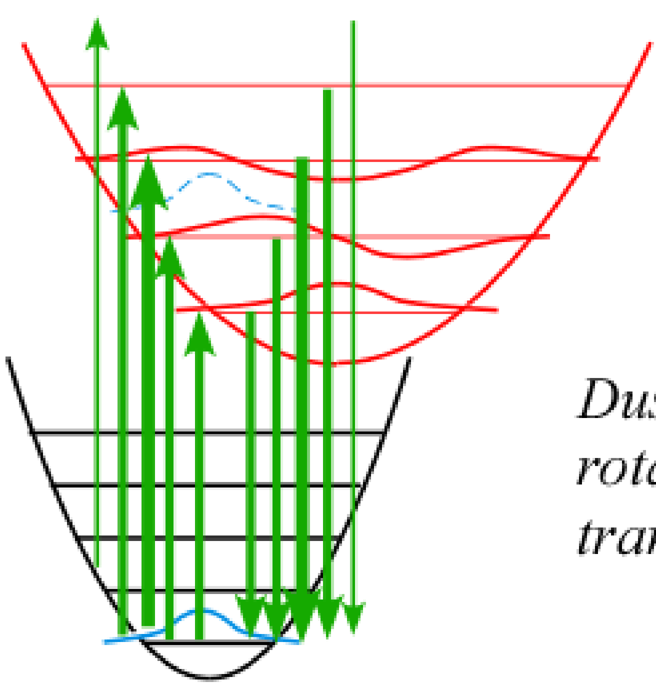
Inter-PES electronic transitions

Vibrational Franck-Condon effects

- Frequency mismatch of PES



- Shape or position mismatch of PES



Duschinsky rotation or translation

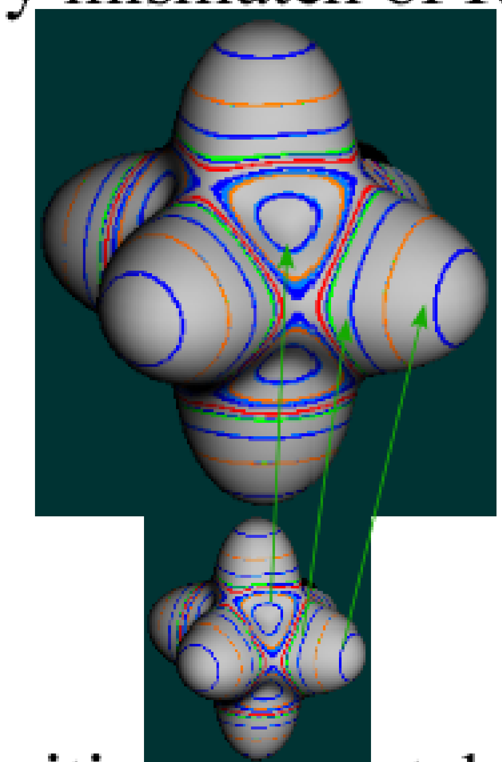
Analogy between Vibronic and Rovibronic

Rotation Energy Surface (RES) Dynamics

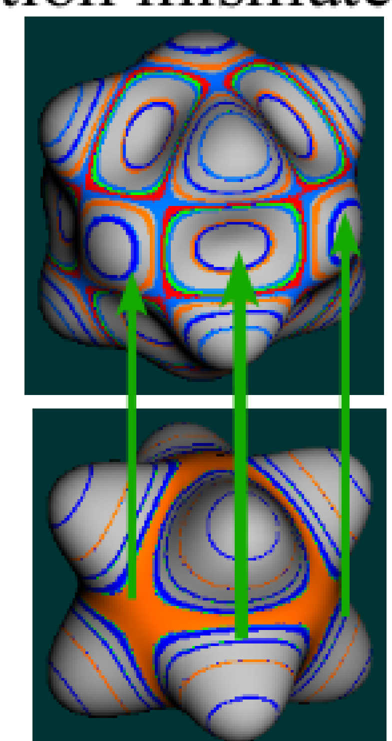
Inter-PES electronic transitions

Rotational "Franck-Condon" effects

- Frequency mismatch of RES



- Shape or position mismatch of RES

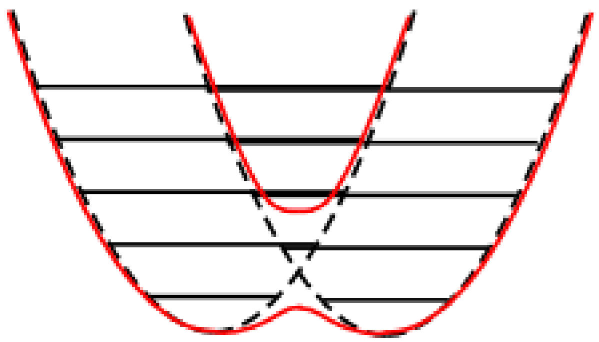


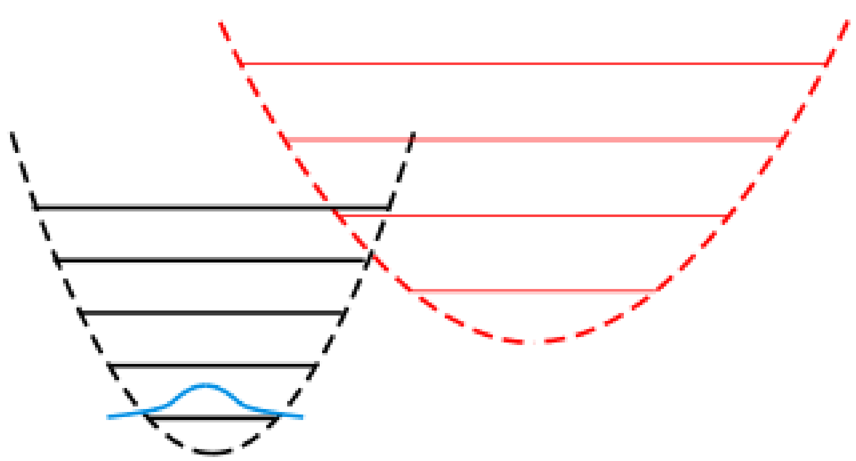
Non-Born-Oppenheimer Surfaces

Strong vibration-electronic mixing

Jahn-Teller-Renner effects

•Multiple and variable conformer minima





Rotation Energy Eigen-Surfaces (REES)

Inter-PES electronic transitions

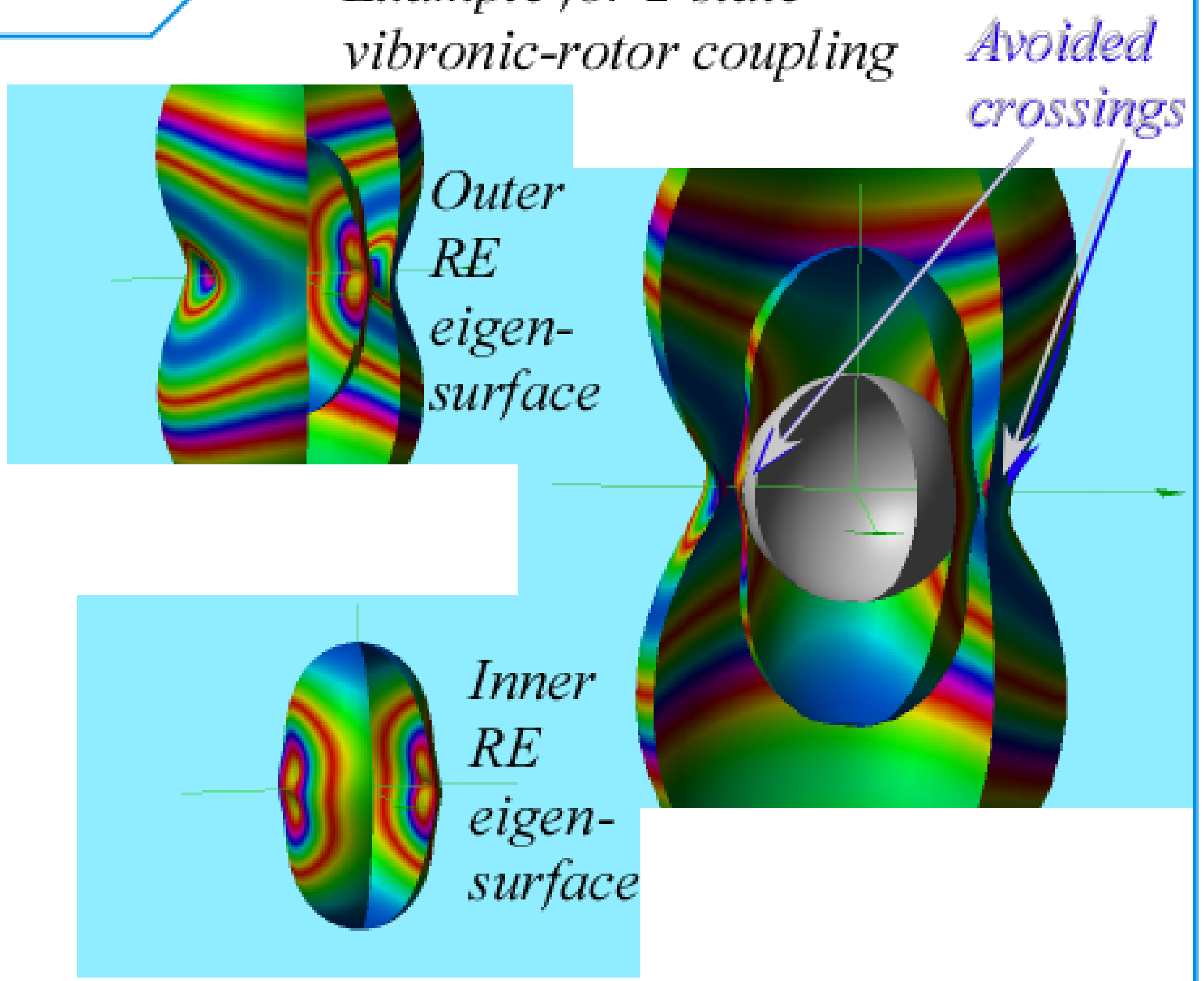
Rotational JTR effects

•Multiple and variable J-axes

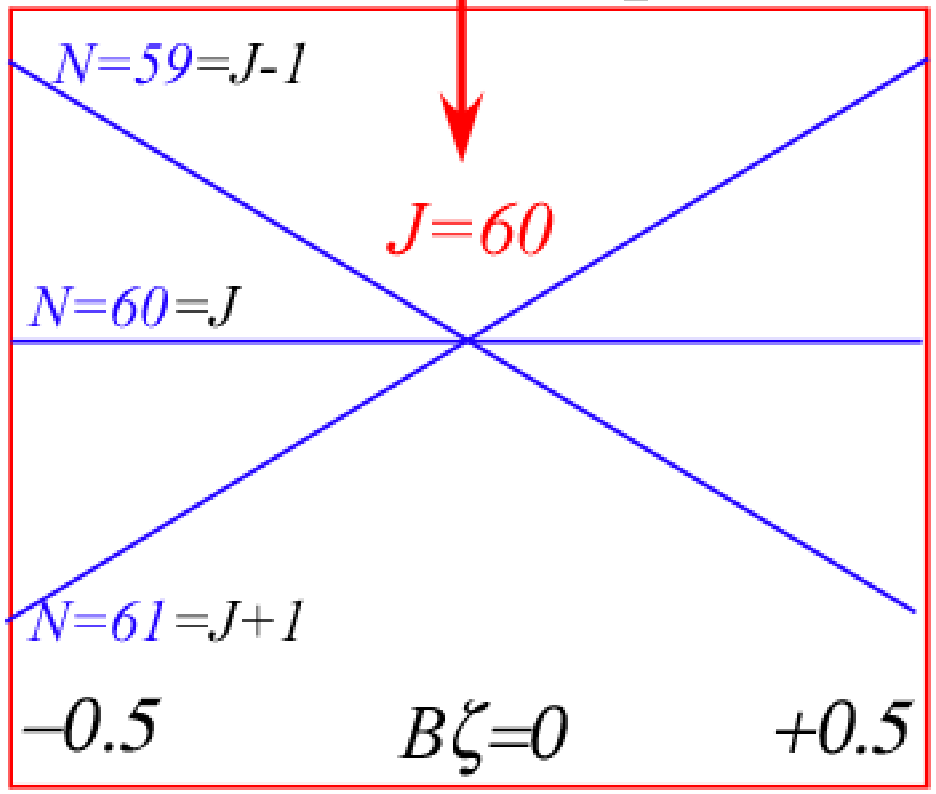
Analogy between

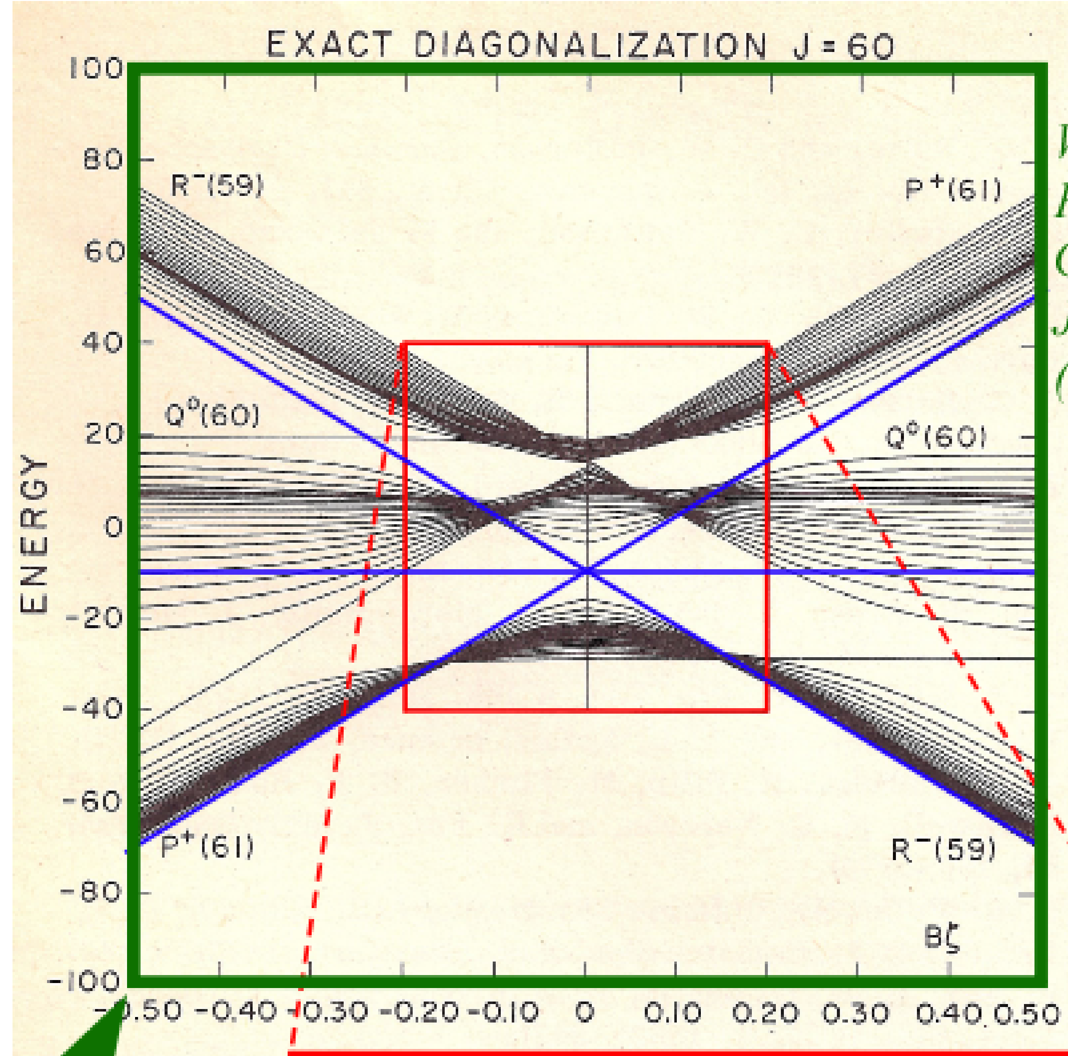
Vibronic and Rovibronic

Example for 2-state vibronic-rotor coupling



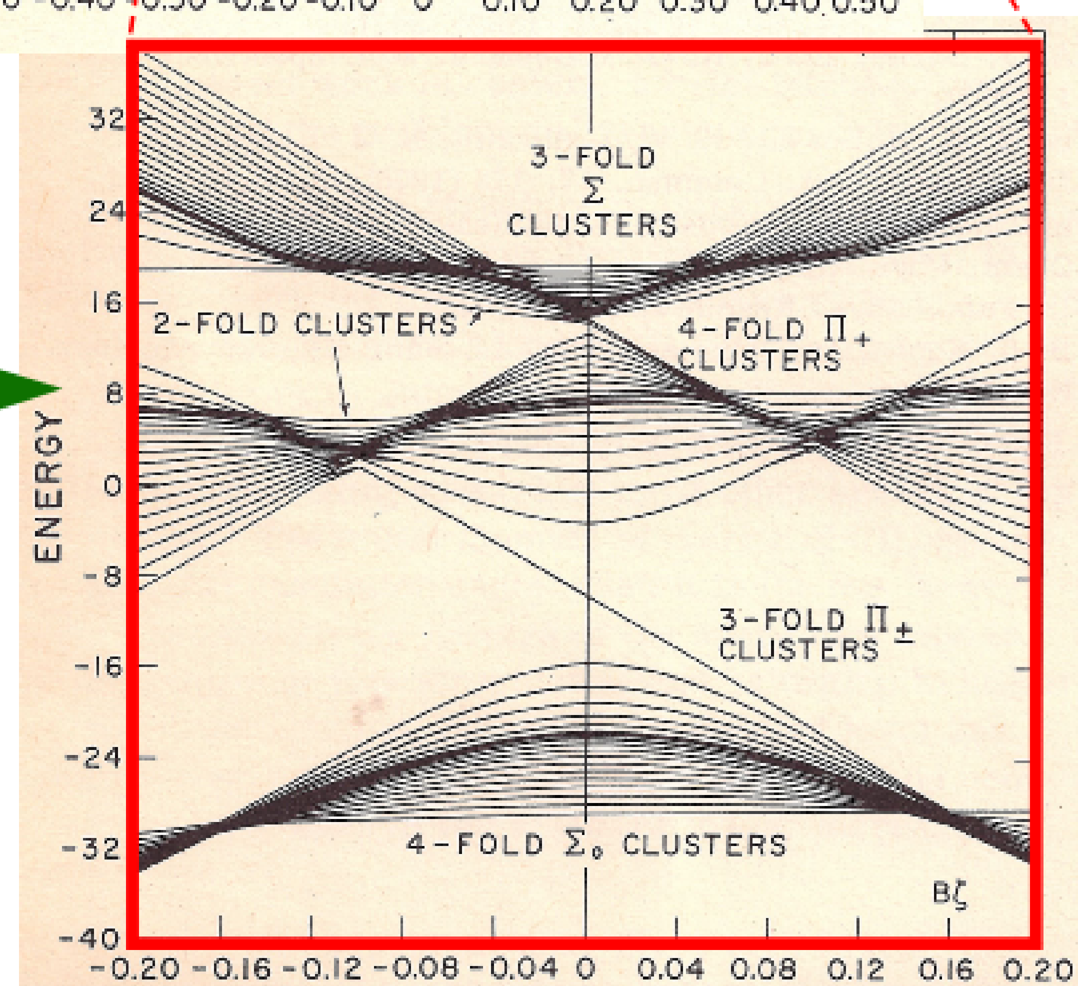
Recall scalar Coriolis
PQR plots vs. $B\zeta$
Here is a *J=60* piece of it:





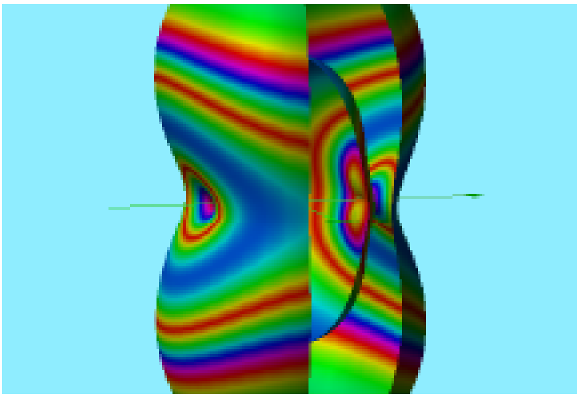
WGH, Patterson, Galbraith JCP 69, 4906 (1978)

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!)

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

$$\qquad\qquad\qquad\qquad\qquad |\Pi+\rangle \quad |\Sigma+\rangle \quad |\Pi-\rangle$$

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

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

Lab-PQR-Basis

$$\qquad\qquad\qquad\qquad |P\rangle|Q\rangle|R\rangle$$

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

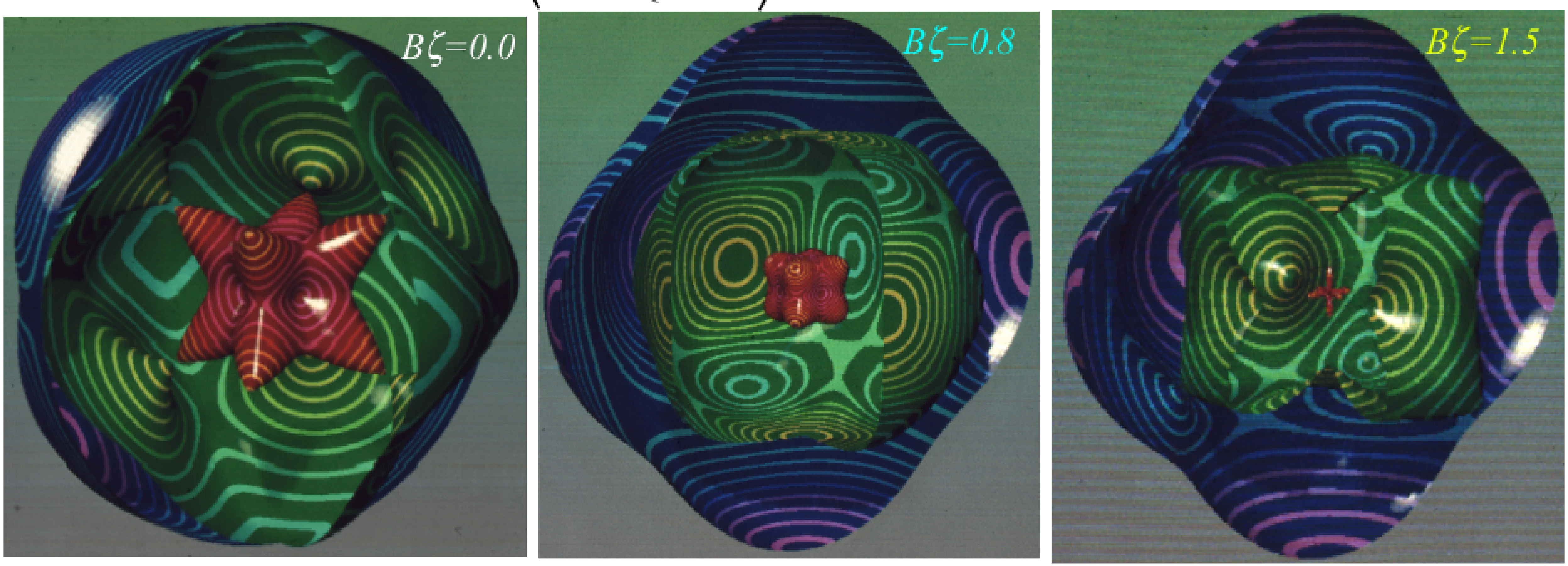
(Either basis should give same REES)

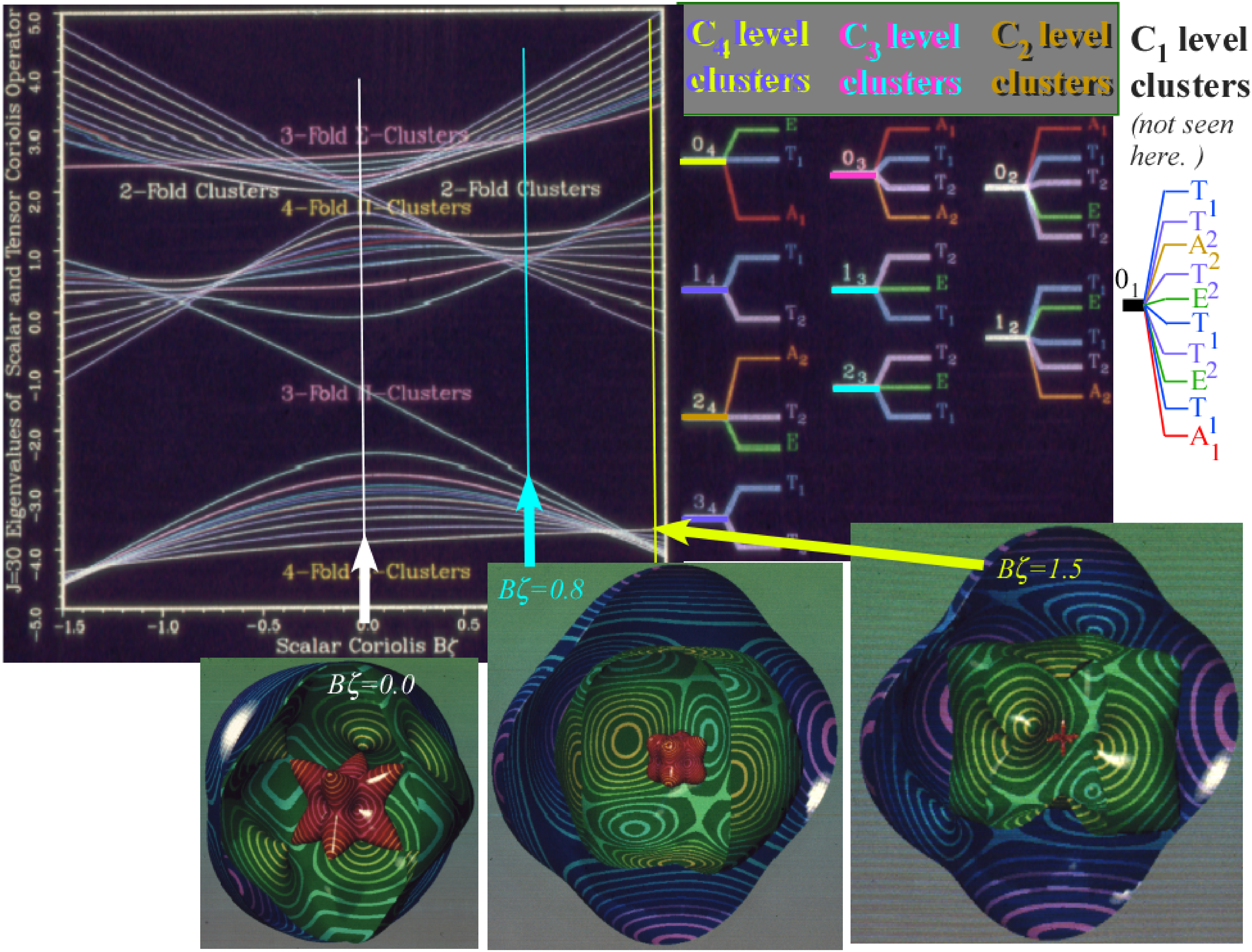
$$+2t_{224}|J|^2\begin{pmatrix}H_{PP} & H_{PQ} & H_{PR}\\ H^*_{PQ} & H_{QQ} & H_{QR}\\ H^*_{RP} & H^*_{QR} & H_{RR}\end{pmatrix}$$

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

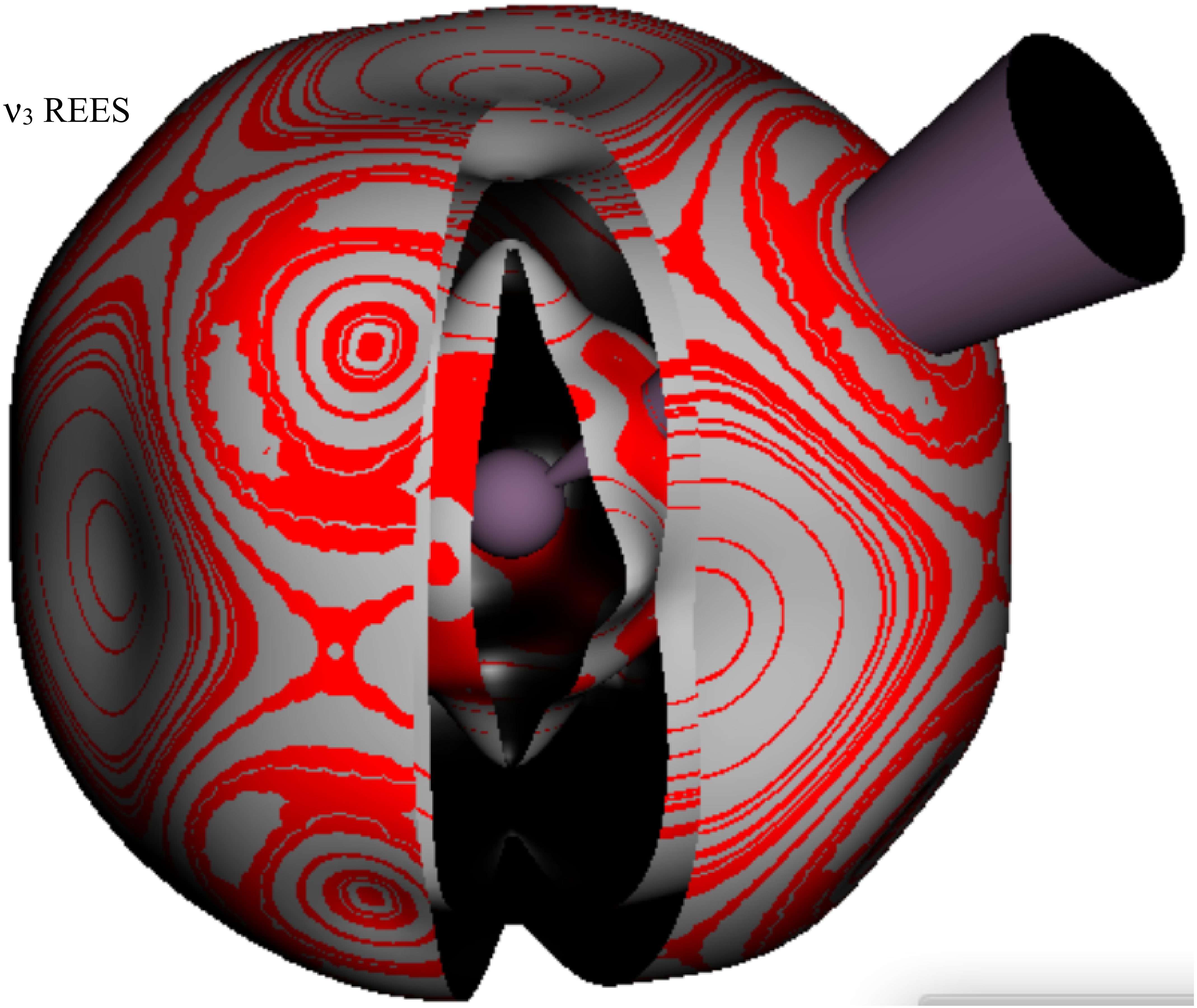
$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

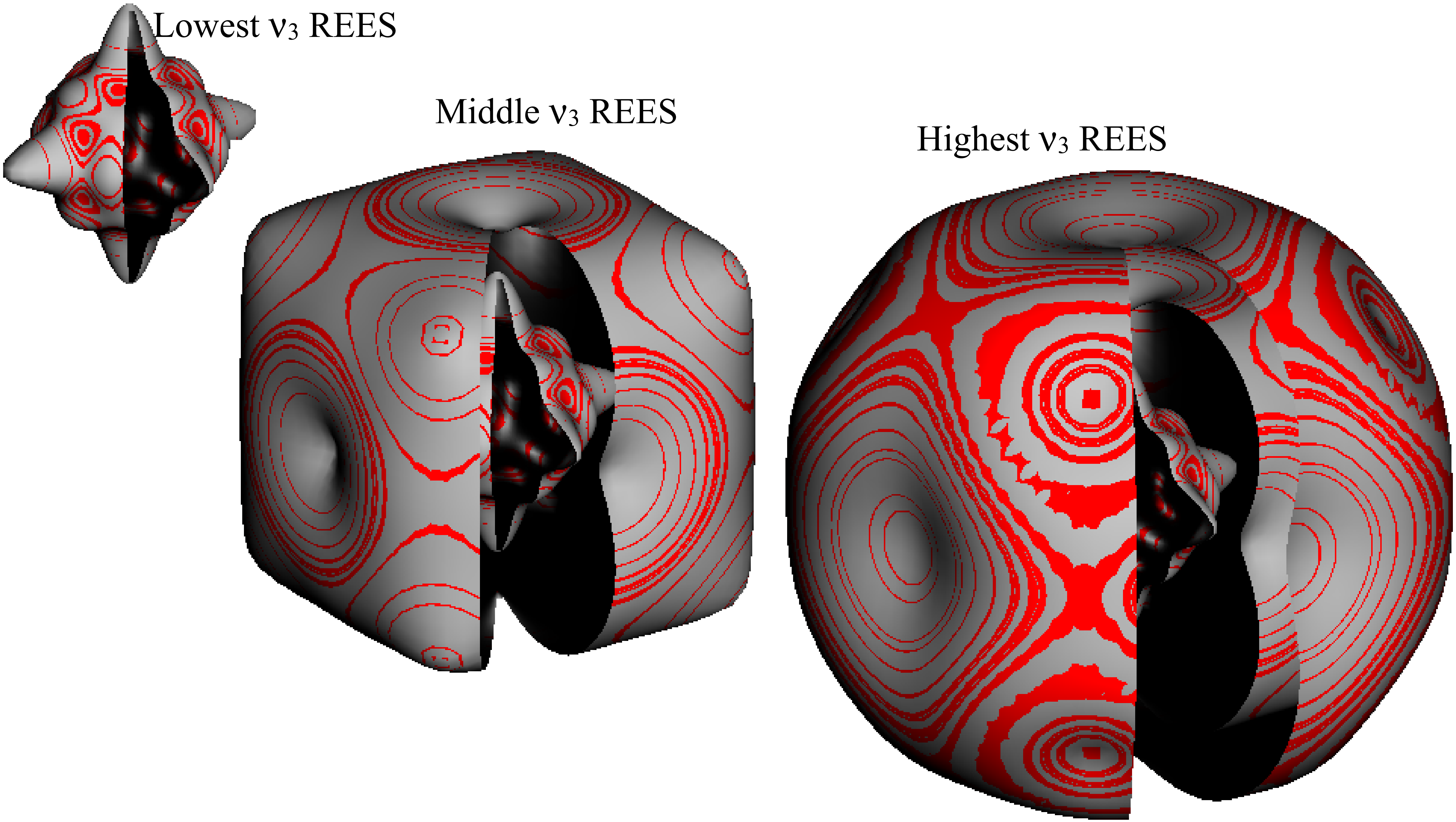
$$H_{PQ}=5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos4\gamma+2i\cos\beta\sin^2\beta\sin4\gamma-1)/4$$




J=30 Eigenvalues of Scalar and Tensor Coriolis Operator
Scalar Coriolis Bζ
3-Fold E-Clusters
2-Fold Clusters
4-Fold II-Clusters
2-Fold Clusters
3-Fold II-Clusters
4-Fold I-Clusters
C4 level clusters
C3 level clusters
C2 level clusters
C1 level clusters
(not seen here.)
Bζ=0.0
Bζ=0.8
Bζ=1.5

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

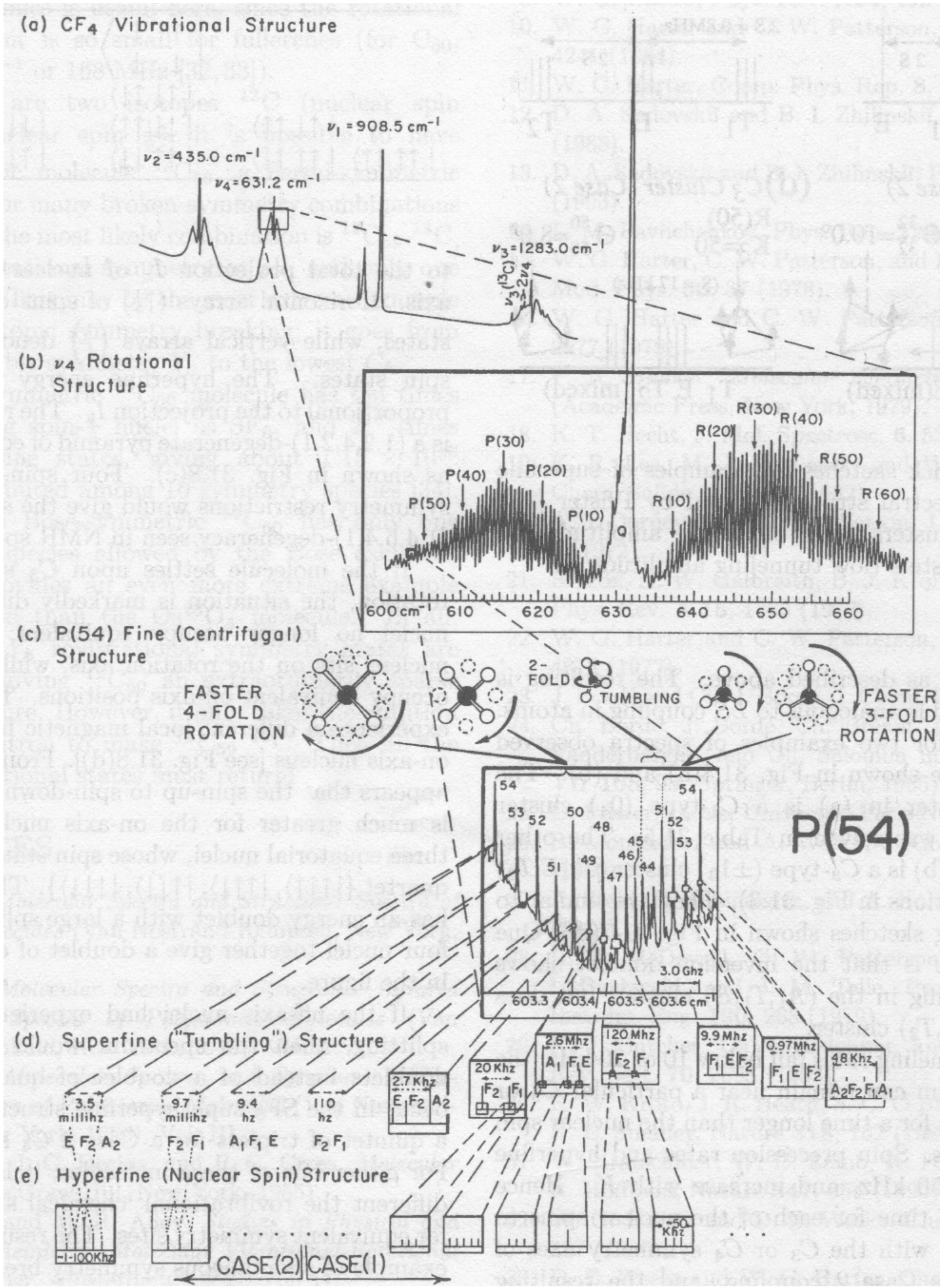
Spherical rotor levels and RES plots

SF_6 spectral fine structure

➡ *CF_4 spectral fine structure*

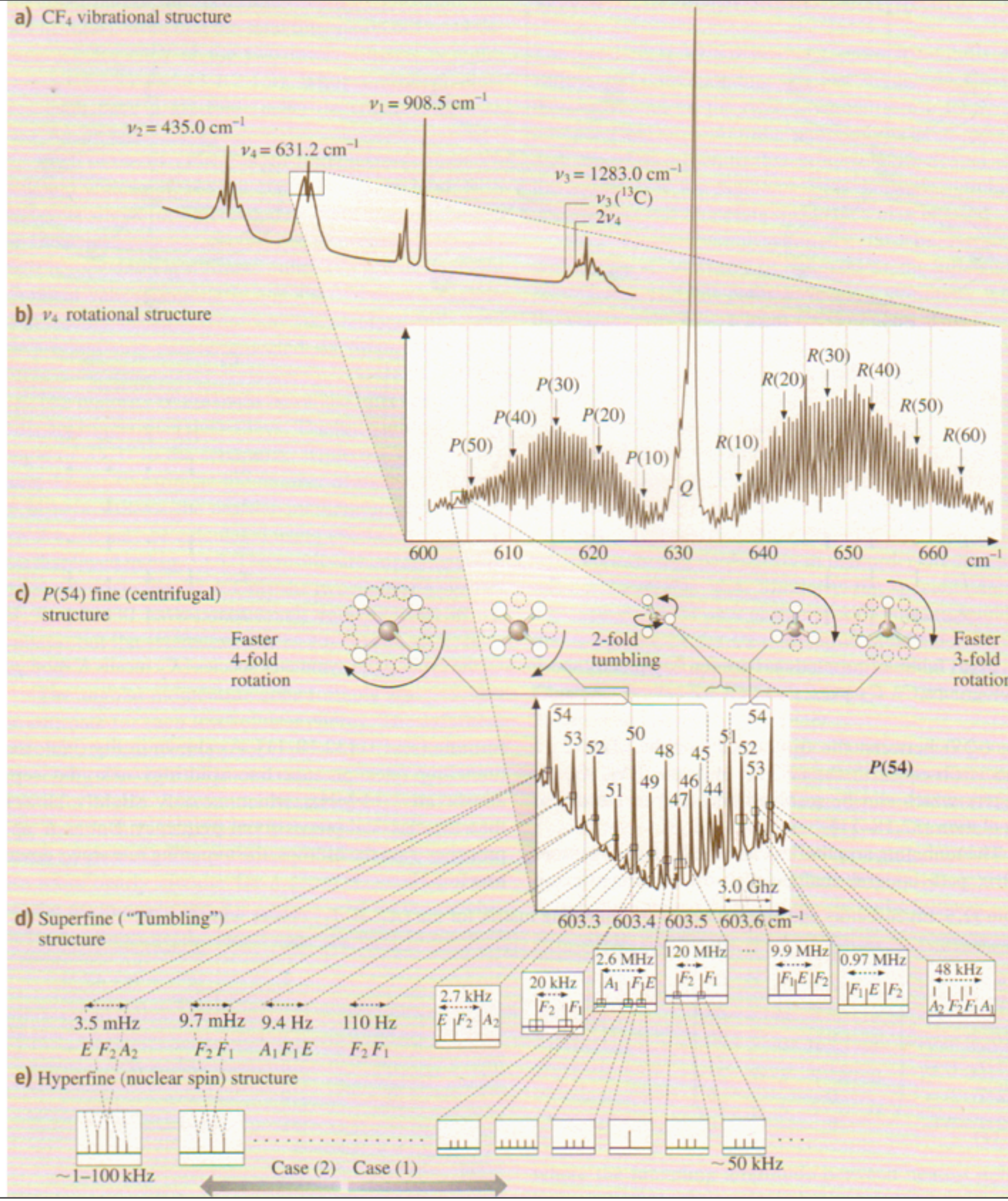
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

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