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

Group Theory in Quantum Mechanics

Lecture 27 (5.03.17)

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,...

$R(3) \supset O, O \supset C_4$ *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) v_4 SF_6 and P(54) v_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

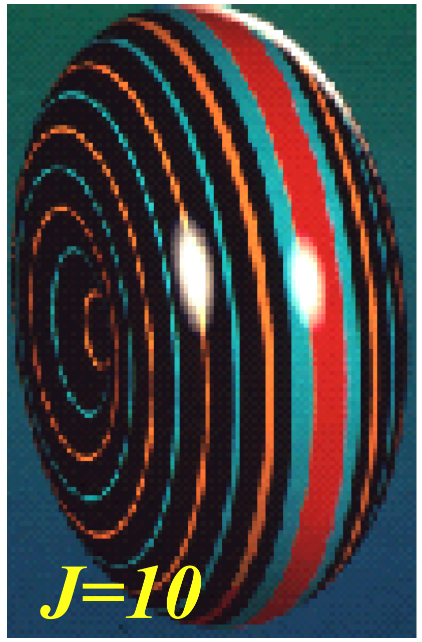
Analogy between PE surface dynamics and RES

Rotational Energy Eigenvalue Surfaces (REES)

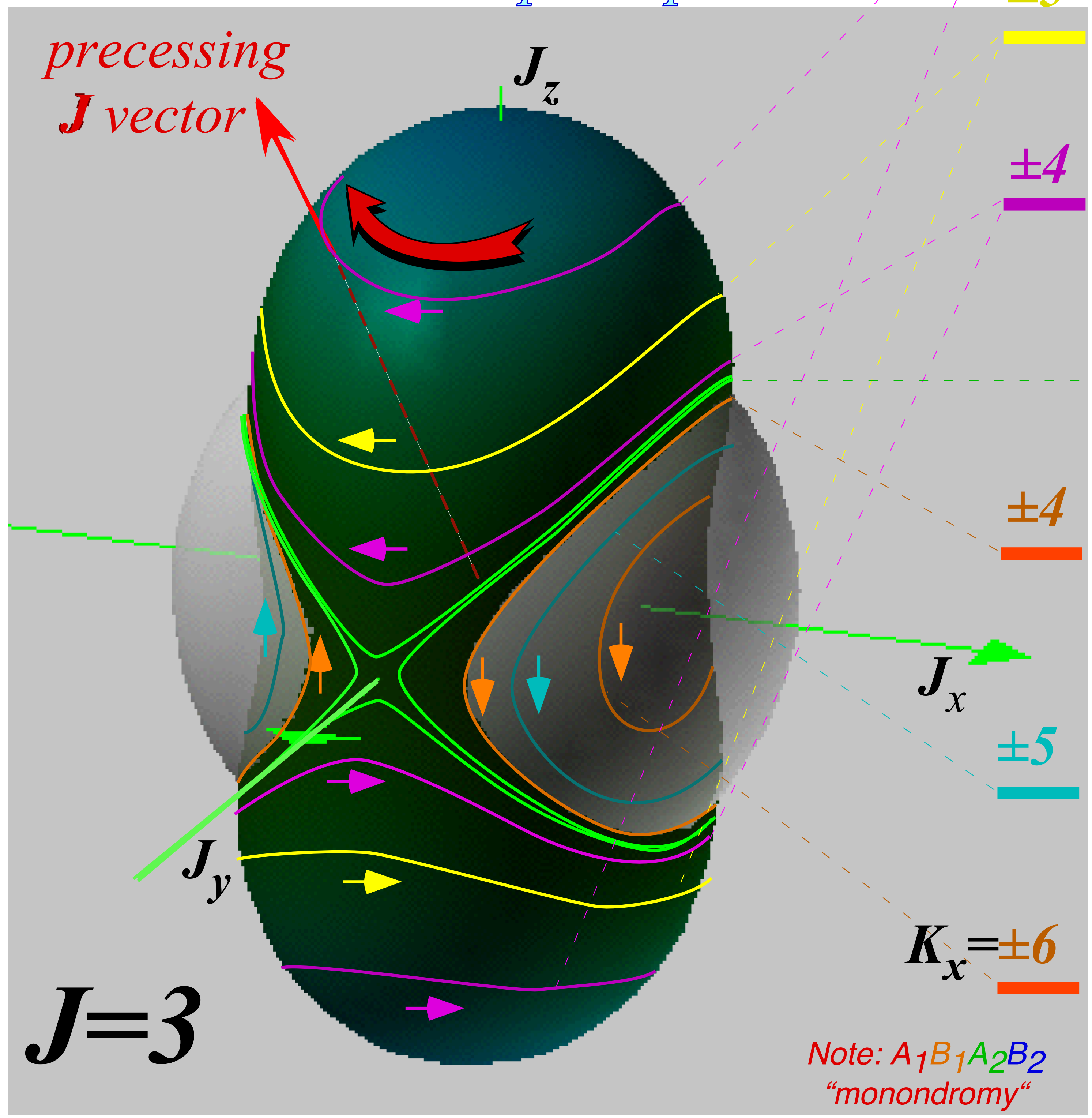
→ *Review: Asymmetric rotor levels of* $\mathbf{H}=A\mathbf{J}_x^2+B\mathbf{J}_y^2+C\mathbf{J}_z^2$ *and RES plots*

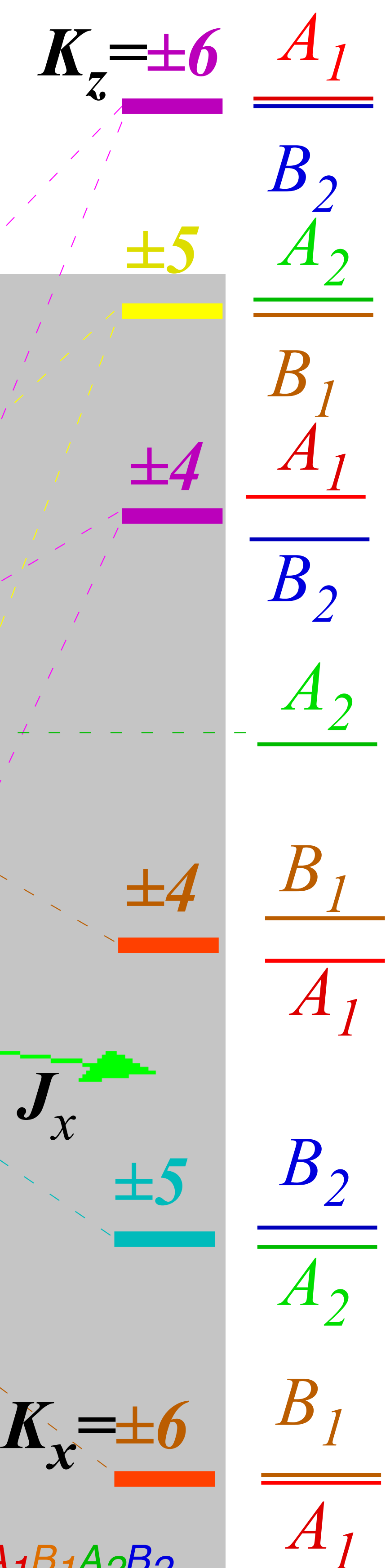
$D_2 \supset C_2$ symmetry correlation

Review: Symmetric vs. Asymmetric rotor levels



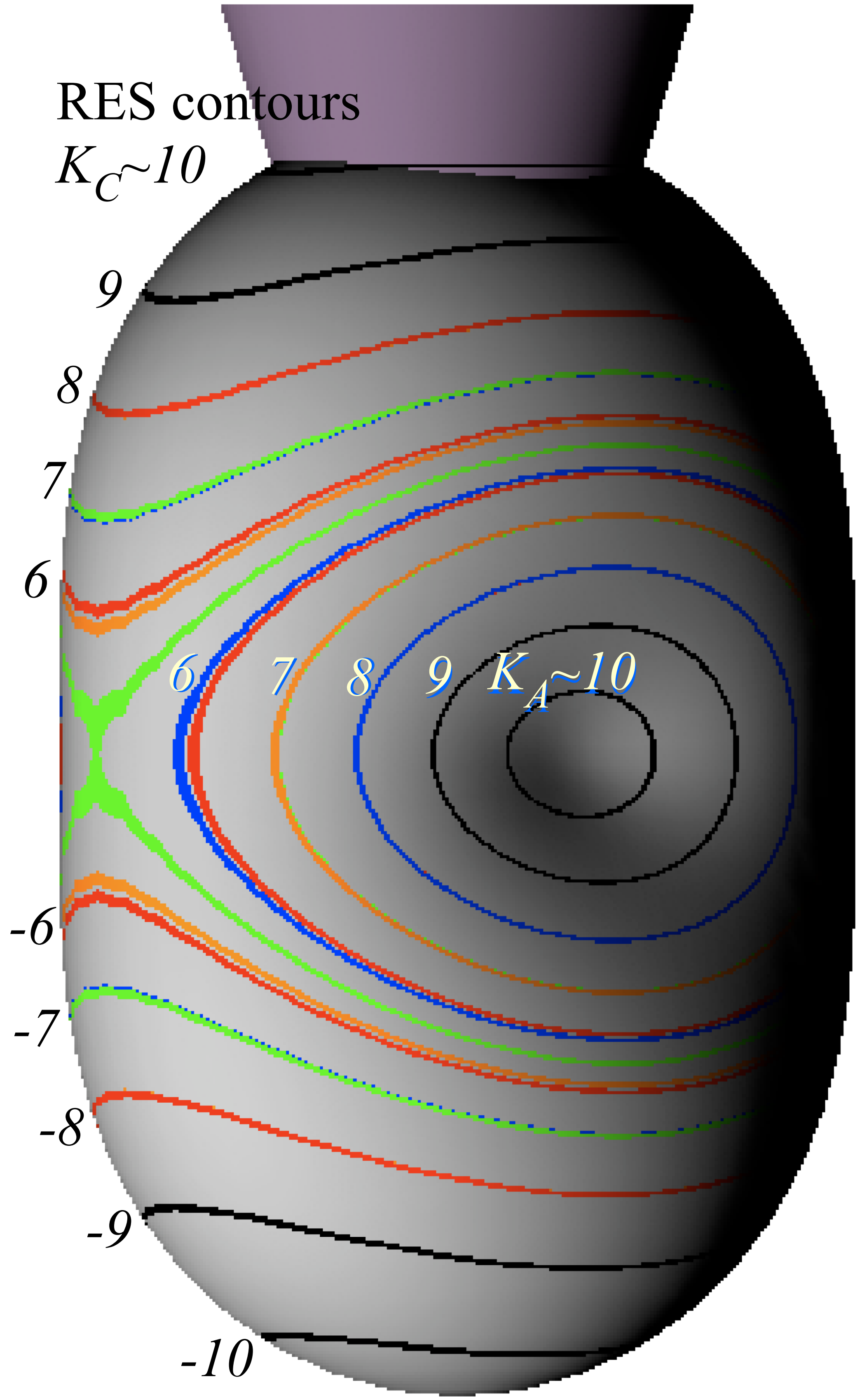
Asymmetric Top Eigensolutions Related to RE Surface and semi-classical J-phase paths





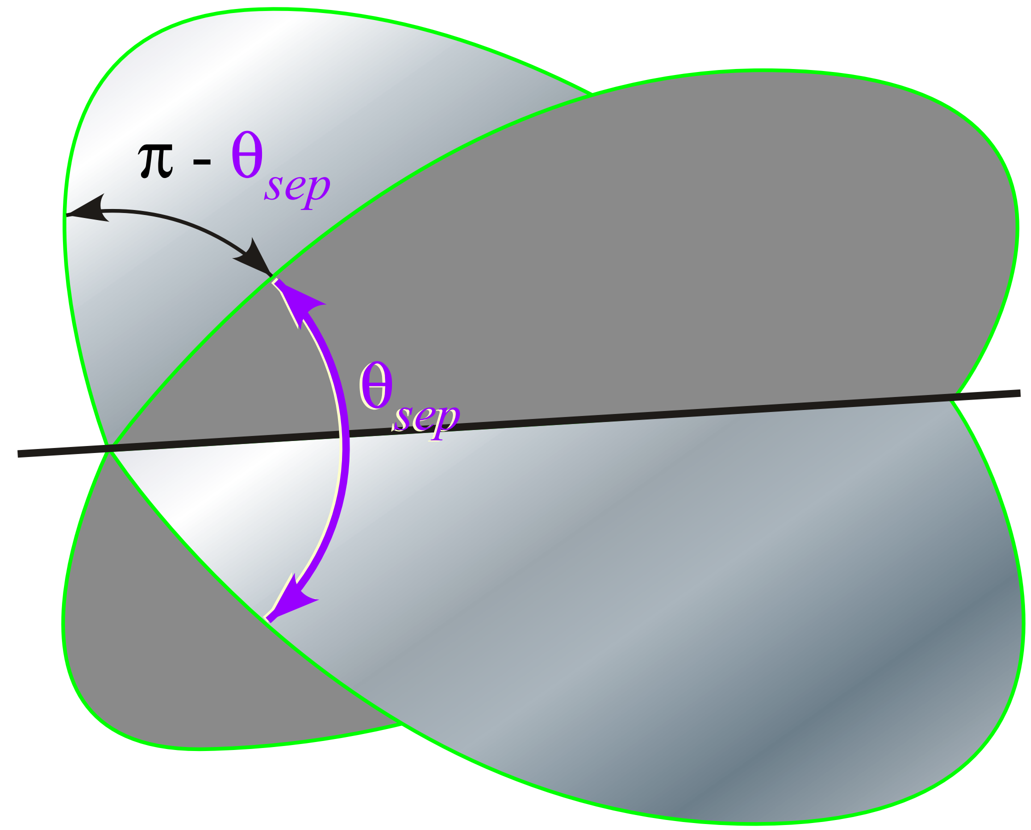
after QTforCA Unit 8. Ch. 25 Fig. 25.4.1

Review: Asymmetric rotor levels

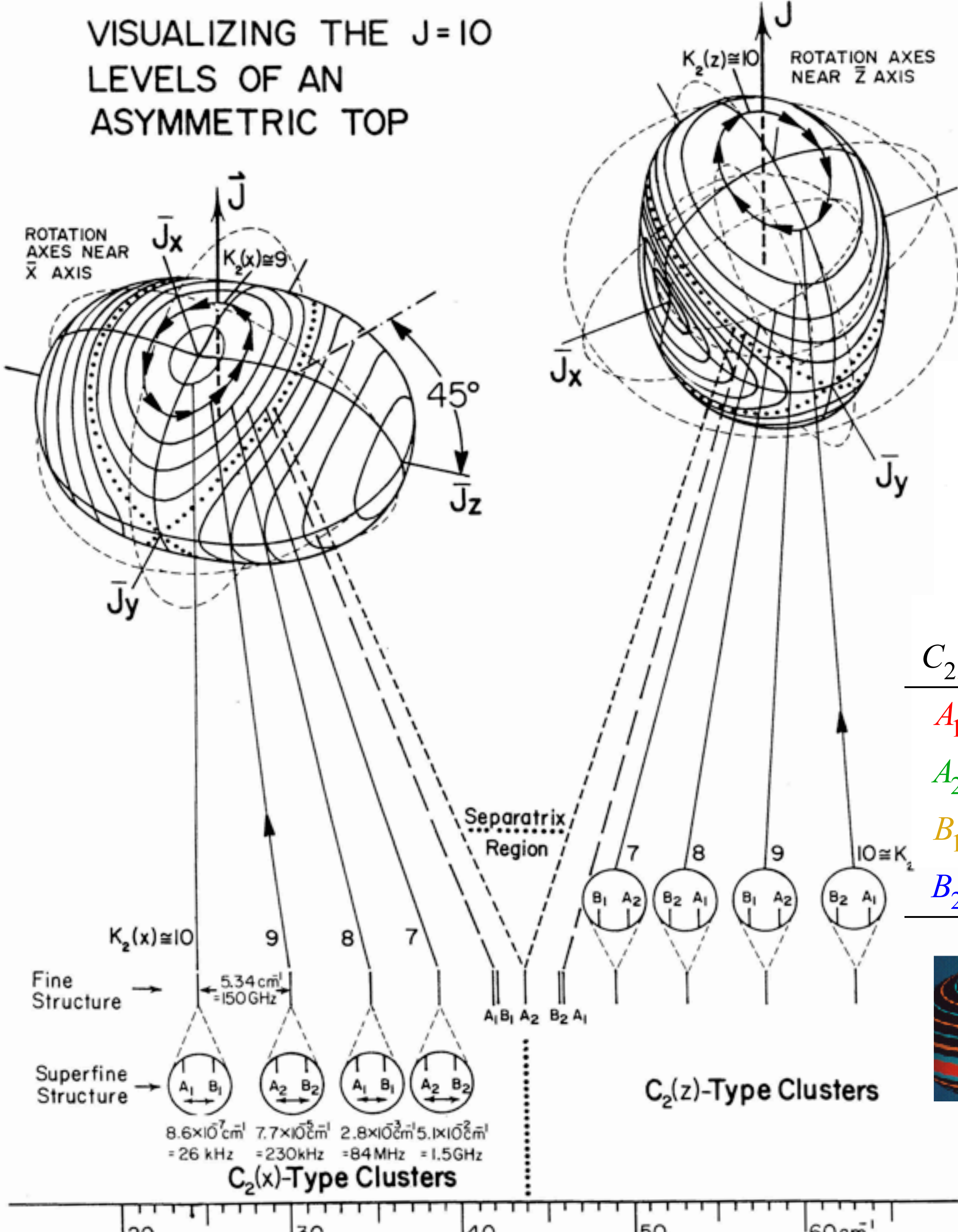


Separatrix circle pair dihedral angle

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



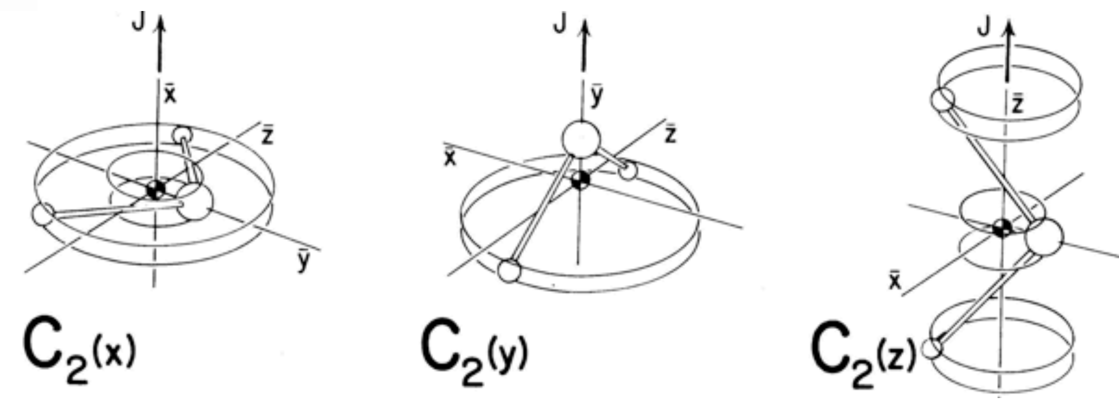
Int.J.Molecular Science 14.(2013) Fig.3 p. 733



D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
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	·

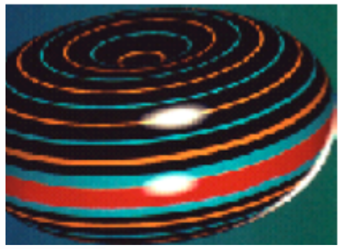


Fig. 25.4.2 *$J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*

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 $1_2=(A_2B_1)$

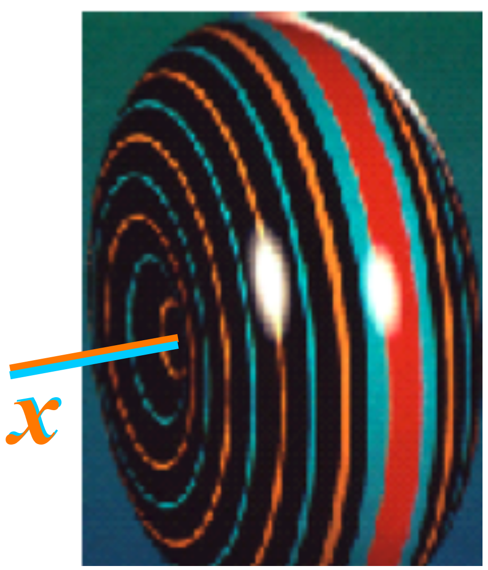
purple $0_2=(A_1B_2)$

for z-prolate axis

orange $0_2=(A_1B_1)$

cyan $1_2=(A_2B_2)$

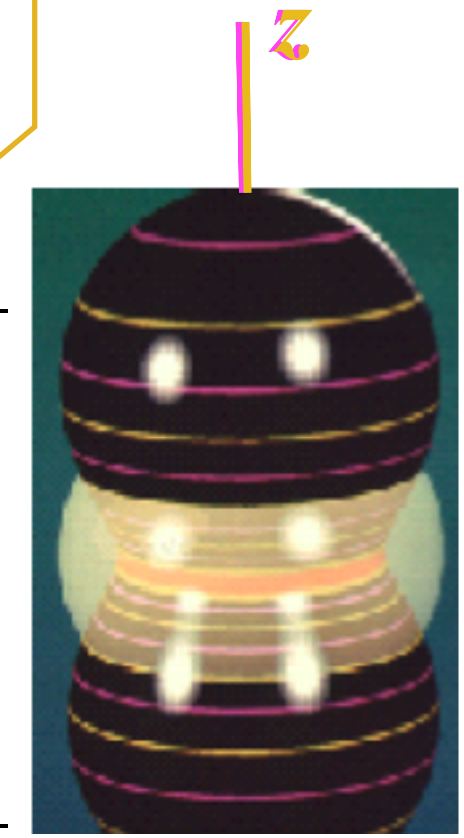
for x-oblate axis



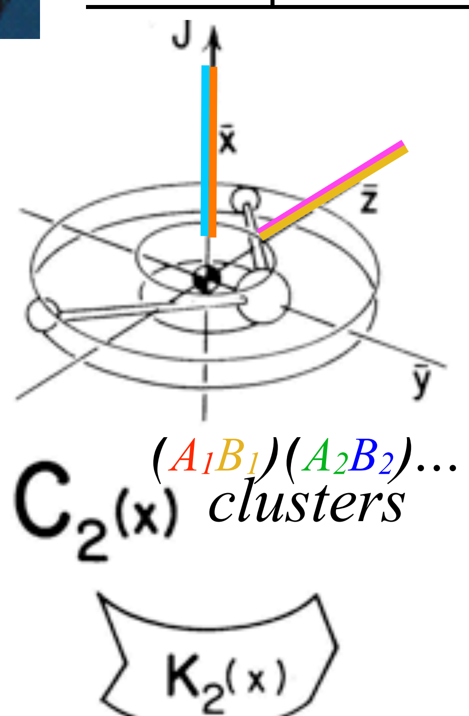
C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

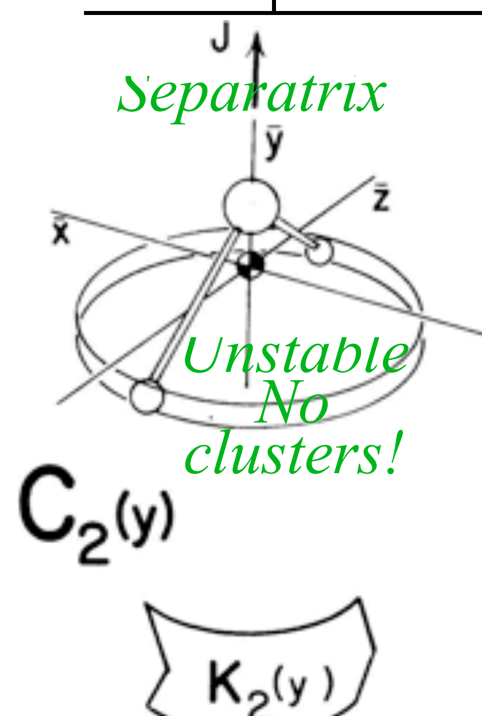
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

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



Review: Asymmetric vs Symmetric rotor levels





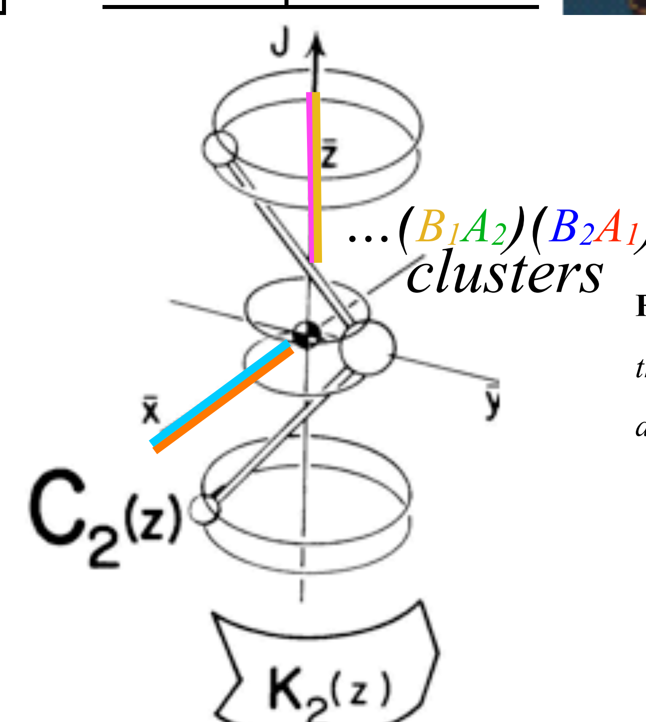


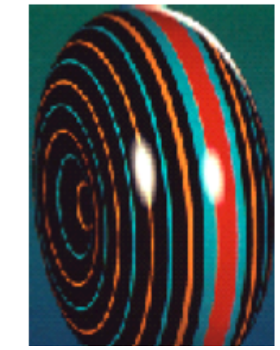
Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*

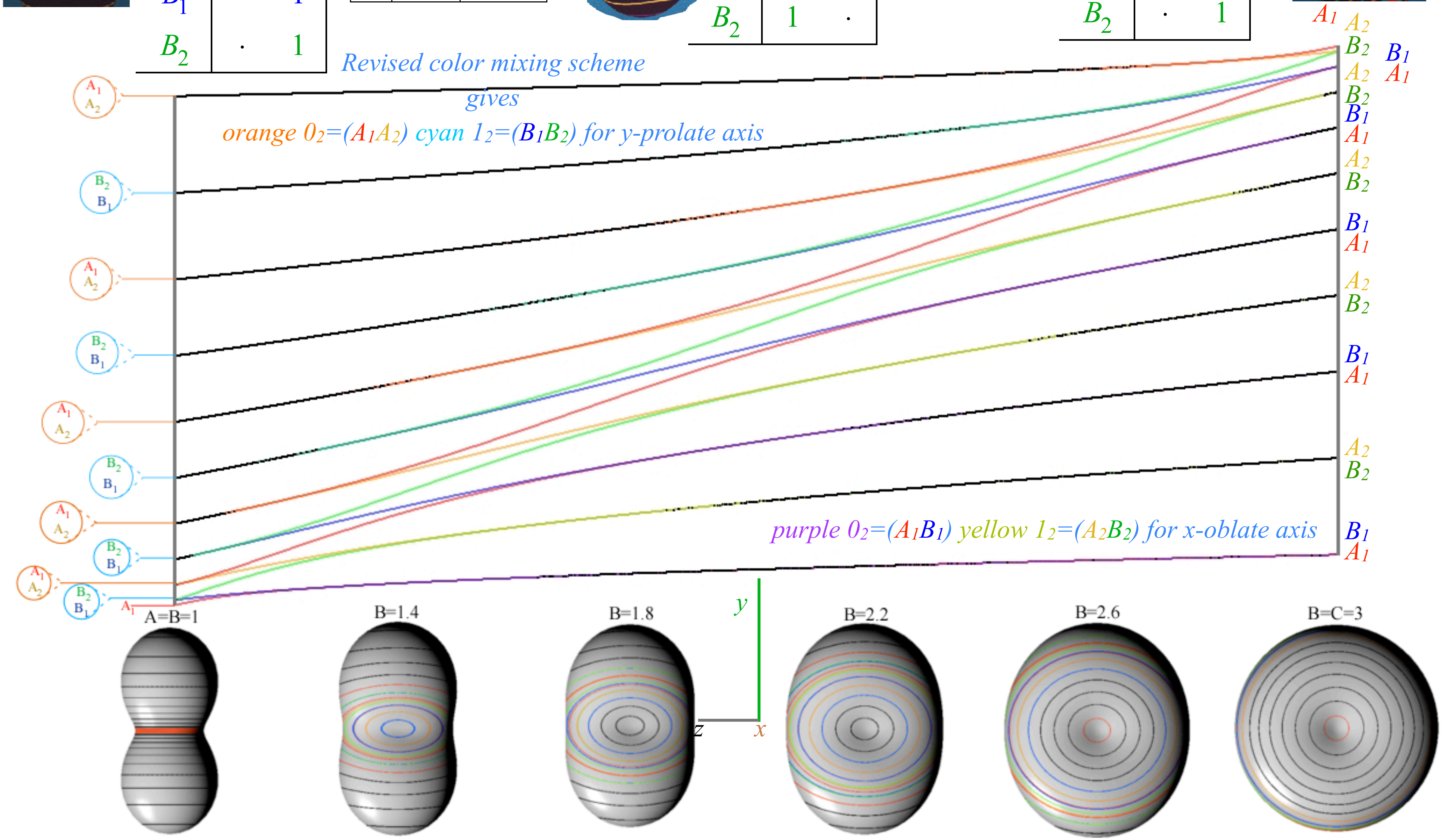
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

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 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, ...

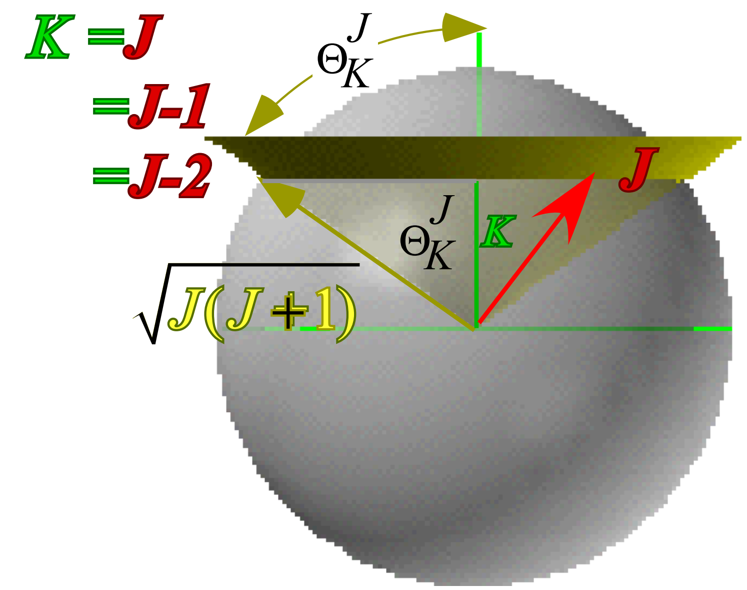
R(3)⊃O symmetry correlation

O⊃C₄ and O⊃C₃ 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

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

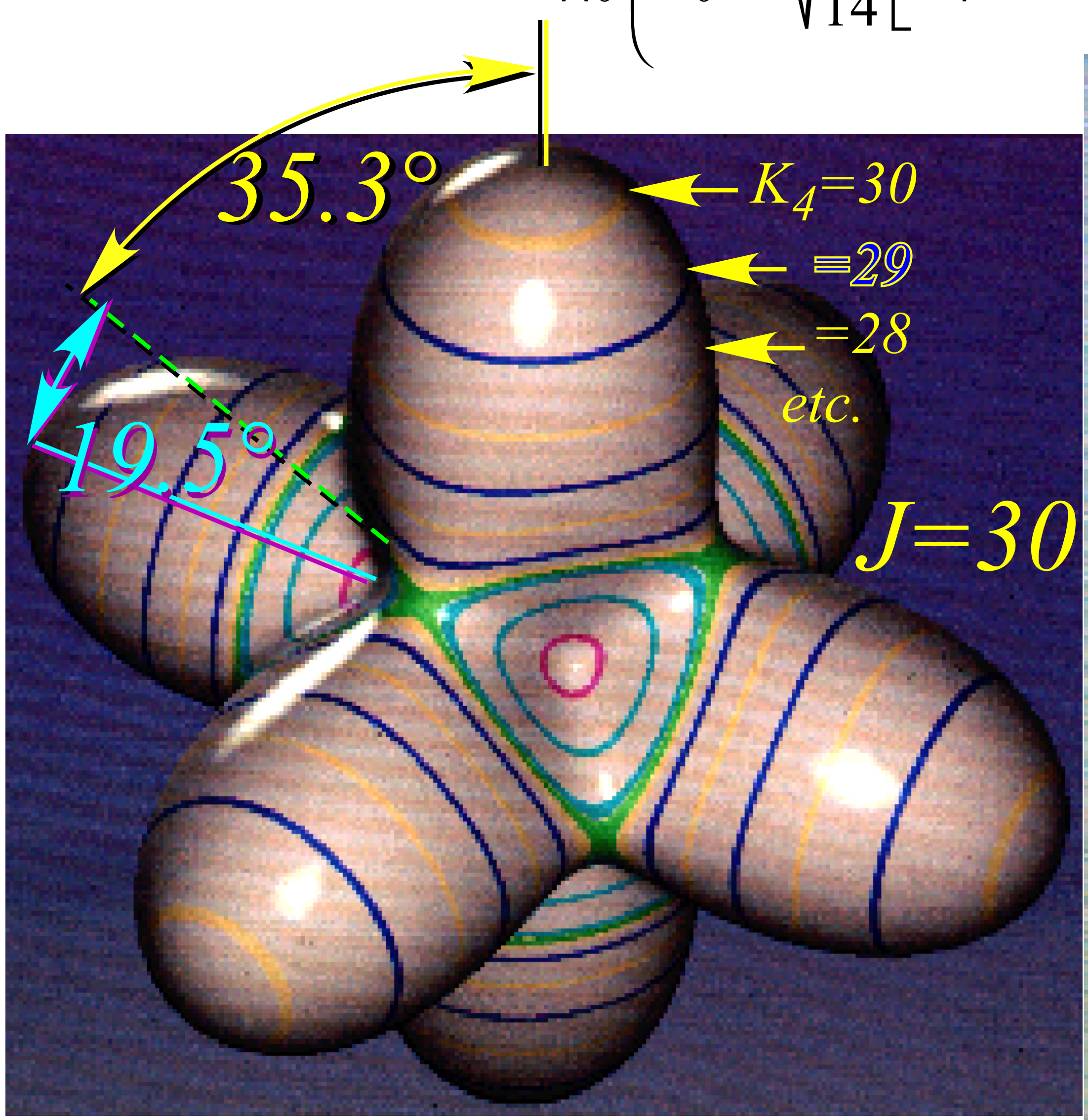


J cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels

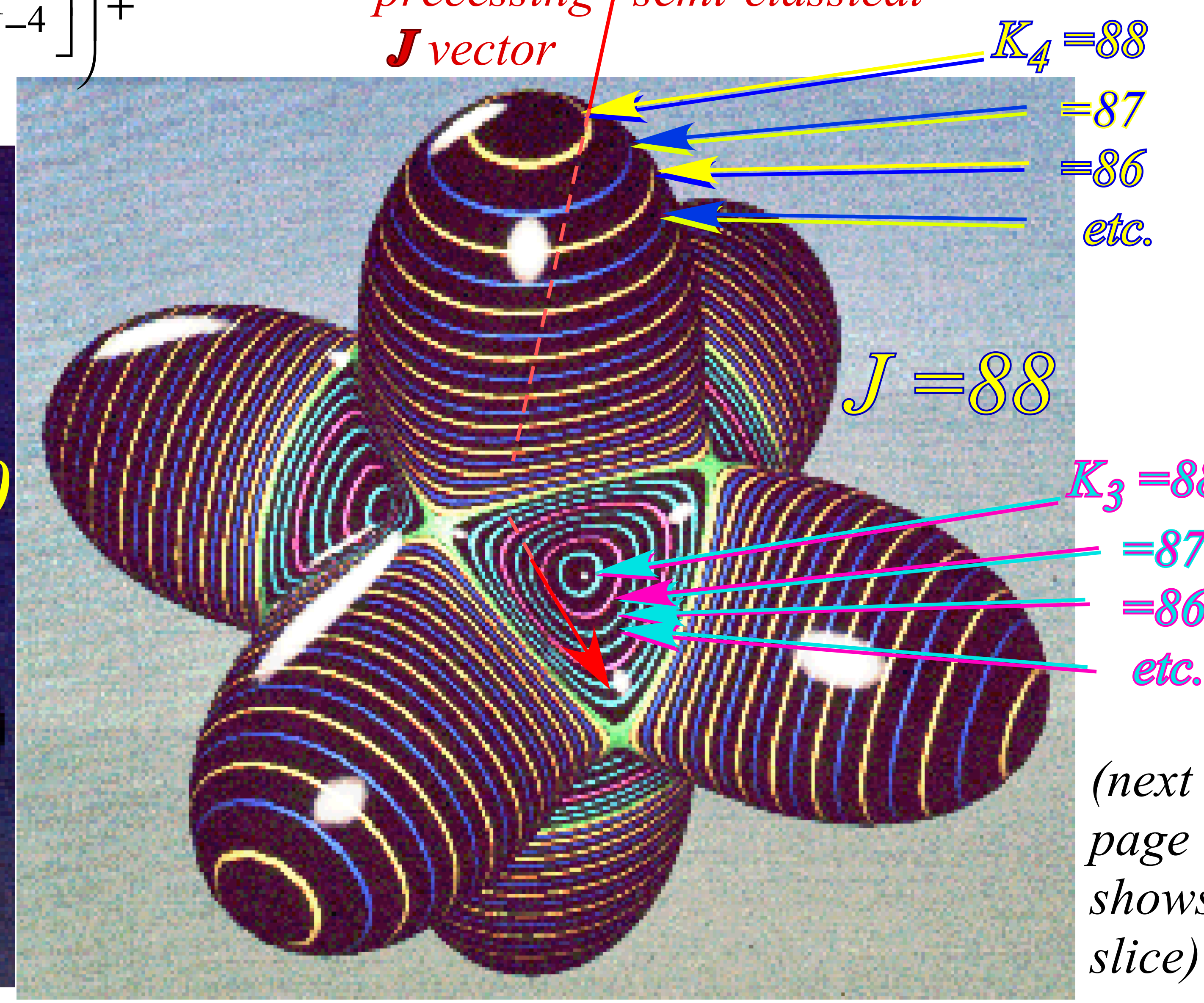
O_h or T_d Spherical Top: (Hecht Ro-vib Hamiltonian 1960)

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

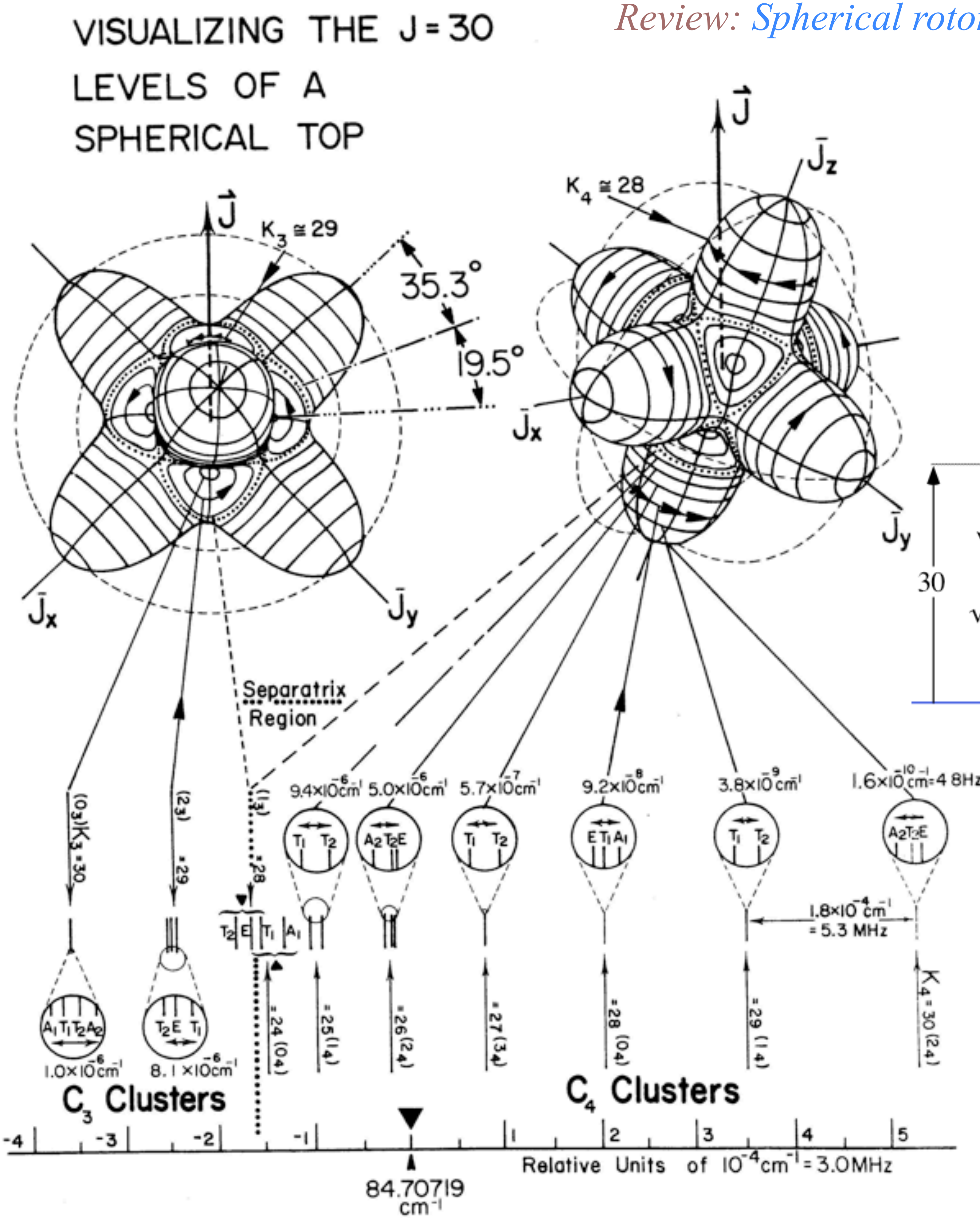
$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$

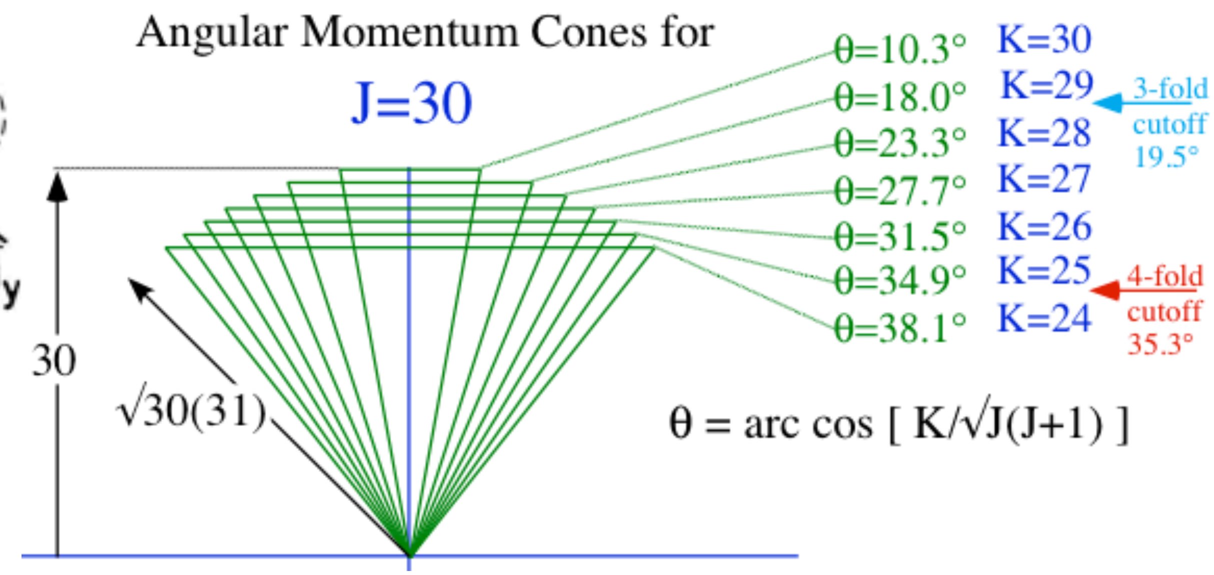


*RE Surface topo-lines track precessing semi-classical **J** vector*



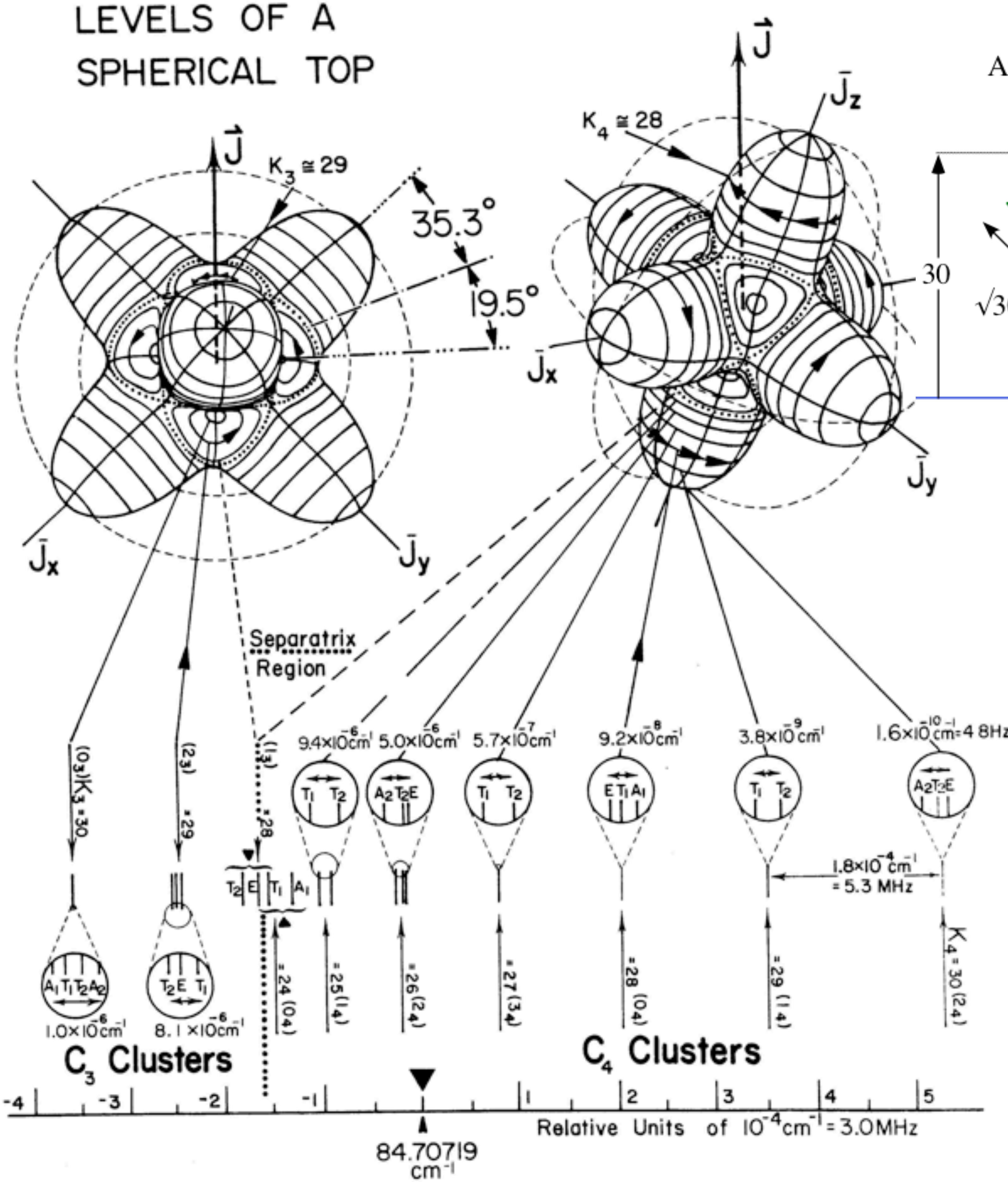
(next page shows slice)

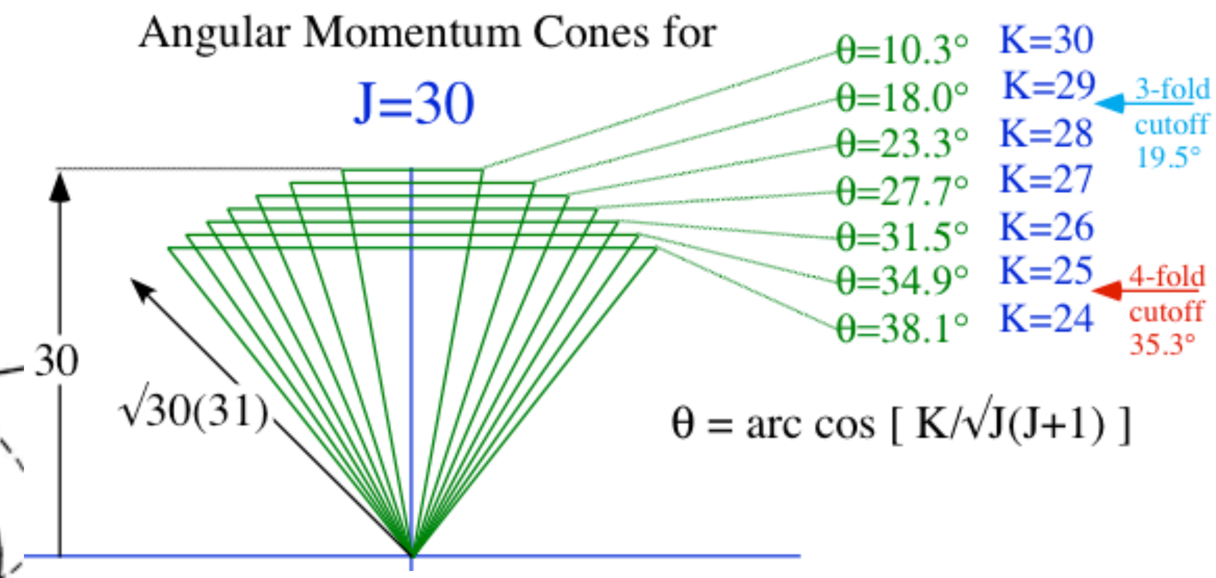

VISUALIZING THE J=30 LEVELS OF A SPHERICAL TOP
J
K3 ≅ 29
35.3°
19.5°
Jx
Jy
Jz
K4 ≅ 28
Separatrix Region
9.4×10^-6 cm^-1
5.0×10^-6 cm^-1
5.7×10^-7 cm^-1
9.2×10^-8 cm^-1
3.8×10^-9 cm^-1
1.6×10^-10 cm^-1 = 4.8Hz
1.8×10^-4 cm^-1 = 5.3 MHz
1.0×10^-6 cm^-1
8.1×10^-6 cm^-1
C3 Clusters
C4 Clusters
Relative Units of 10^-4 cm^-1 = 3.0MHz
84.70719 cm^-1


Angular Momentum Cones for
J=30
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
√30(31)
θ = arc cos [K/√J(J+1)]

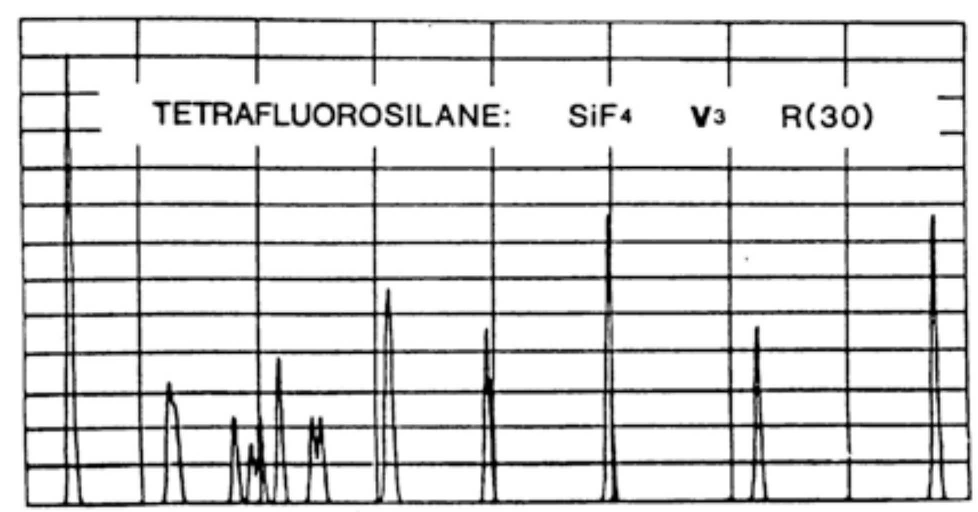
Review: Spherical rotor levels and spectra

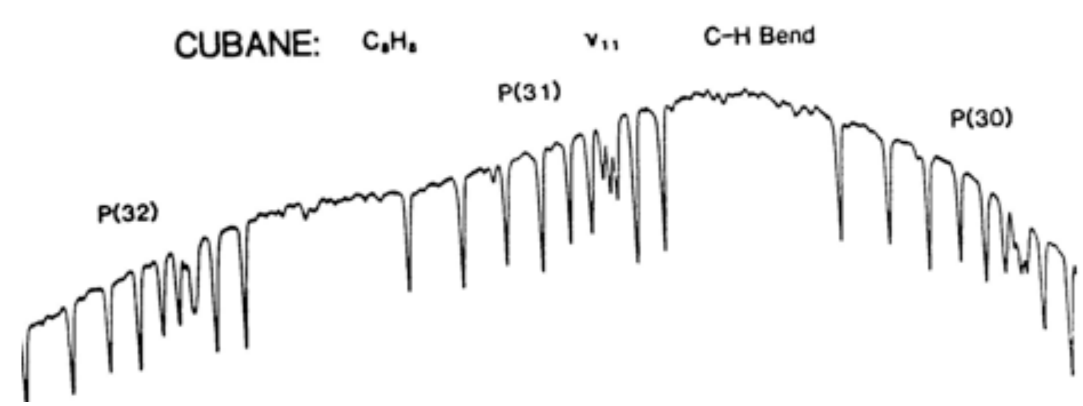
VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



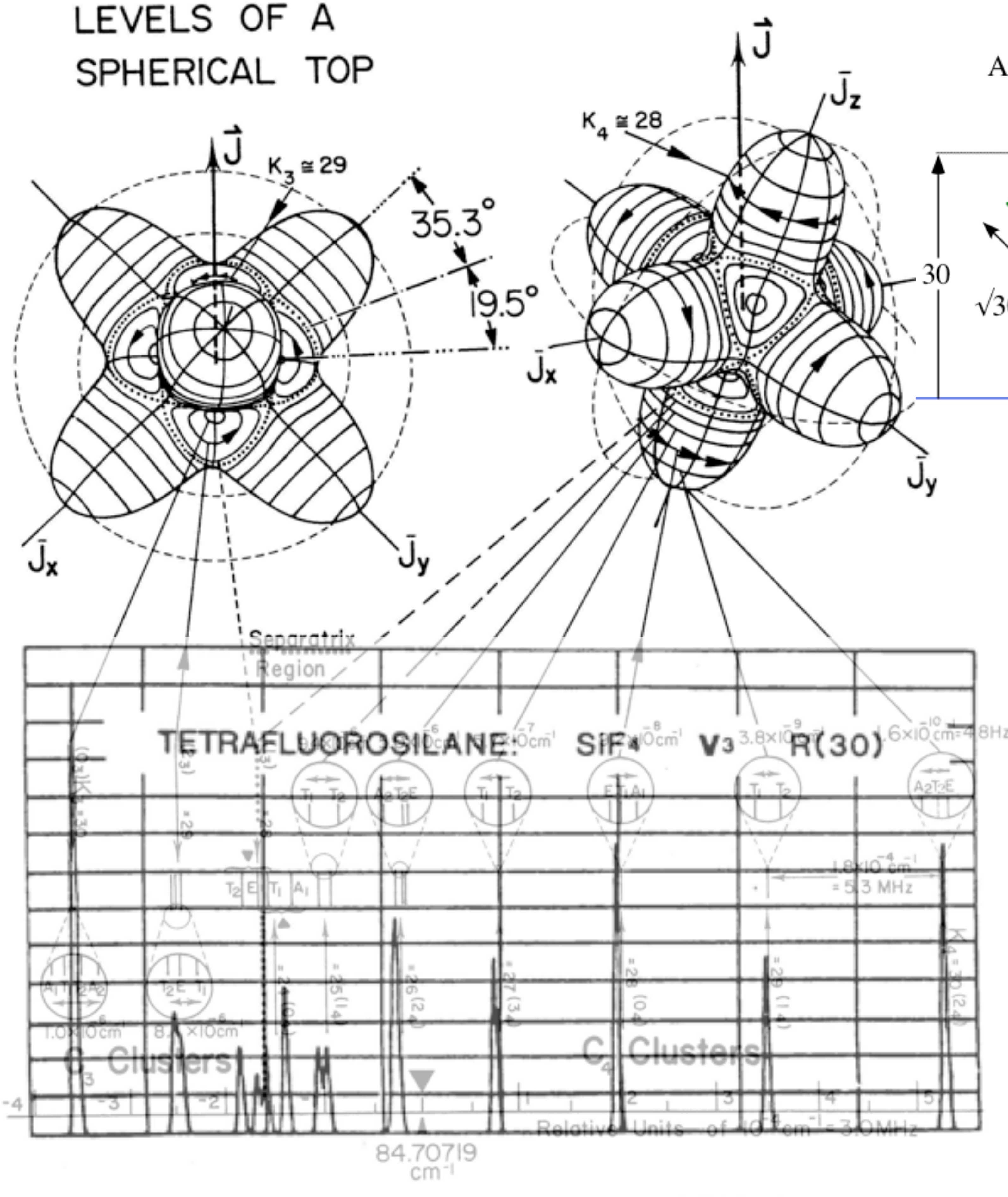


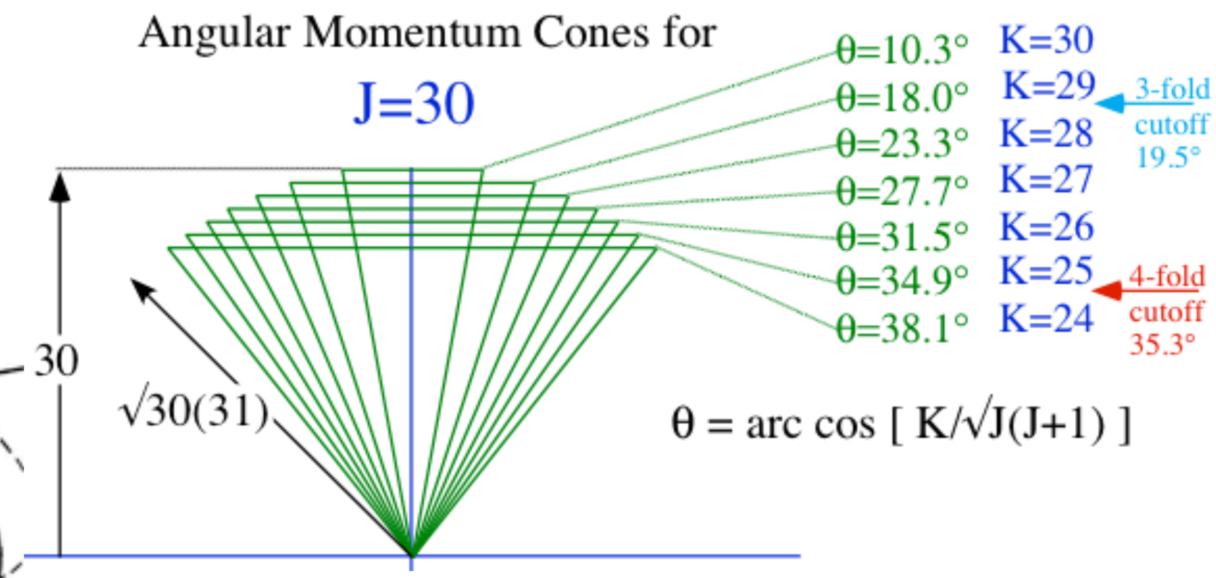
Two molecular examples: SiF_4 and C_8H_8



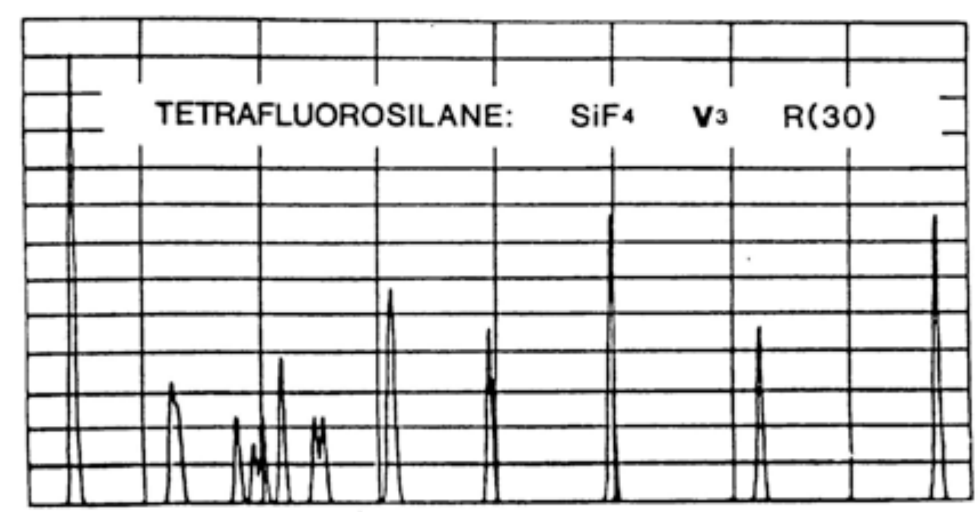


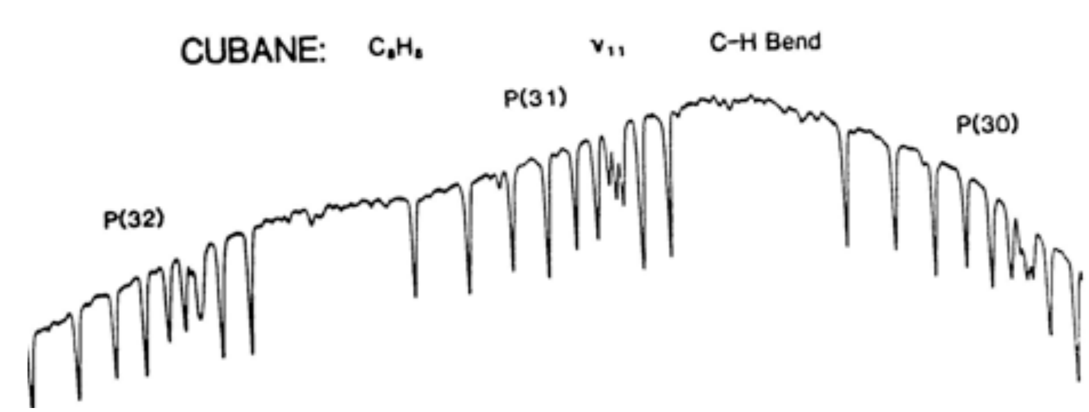
VISUALIZING THE J=30 LEVELS OF A SPHERICAL TOP





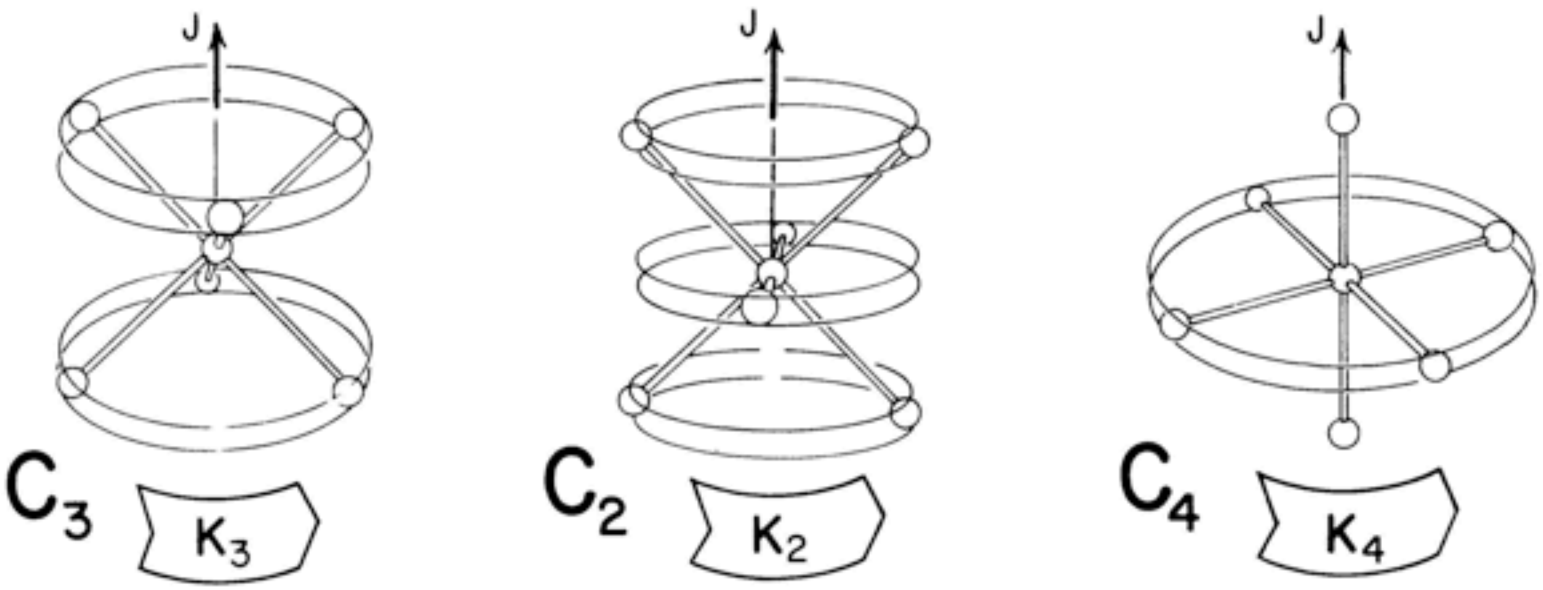
Two molecular examples: SiF_4 and C_8H_8





Previous page: QTforCA Unit 8. Ch. 25 Fig. 25.4.9

Fig. 25.4.9 *Infrared spectra showing fine structure clusters. Tetrafluorosilane (SiF_4) spectrum from a ν_3 R(30) transition ____.*
[After C. W. Patterson, R. S. McDowell, N. G. Nereson, B. J. Krohn, J. S. Wells, and F. R. Peterson, J. Mol. Spectrosc. ***91****, 416 (1982).*
[Cubane (C_8H_8) spectrum from ν_{11} P(30), P(31), and P(32), transitions; cubane (C_8H_8) spectrum from ν_{12} R(36), transition.
[After A. S. Pine, A. G. Maki, A. G. Robiette, B. J. Krohn, J. K. G. Watson, and Th Urbanek, J. Am. Chem. Soc., ***106****, 891 (1984).]*



	0_3	1_3	2_3
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

	0_2	1_2
A_1	1	·
A_2	·	1
E	1	1
T_1	1	2
T_2	2	1

	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

Fig. 25.4.7 *Different choices of rotation axes for octahedral rotor corresponding to local symmetry C_3, C_2, and C_4. Tables correlate global octahedral symmetry species with the local ones.*

QTforCA Unit 8. Ch. 25 Fig. 25.4.7

Review: *Spherical rotor levels and RES plots*

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

➡ $R(3) \supset O$ *symmetry correlation*

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

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

$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.384)

	Trace $\mathscr{D}^l(\omega 00)$					Single Electron Orbital Spectroscopic Labeling
	$\omega = 0°$	$\omega = 120°$	$\omega = 180°$	$\omega = 90°$	$\omega = 180°$	
$l = 0$	1	1	1	1	1	s_g
1	3	0	−1	1	−1	P_u
2	5	−1	1	−1	1	d_g
3	7	1	−1	−1	−1	f_u
4	9	0	1	1	1	g_g
5	11	−1	−1	1	−1	h_u
6	13	1	1	−1	1	i_g
7	15	0	−1	−1	−1	k_u
8	17	−1	1	1	1	l_g
9	19	1	−1	1	−1	m_u
10	21	0	1	−1	1	n_g
11	23	−1	−1	−1	−1	o_u
12	25	1	1	1	1	q_g
13	27	0	−1	1	−1	r_u
14	29	−1	1	−1	1	t_g
15	31	1	−1	−1	−1	u_u
16	33	0	1	1	1	
17	35	−1	−1	1	−1	
18	37	1	1	−1	1	
19	39	0	−1	−1	−1	
20	41	−1	1	1	1	

(5.6.5a)

	Frequency of O Irreps					
	f^{A_1}	f^{A_2}	f^{E}	f^{T_1}	f^{T_2}	
$l = 0$	1	·	·	·	·	A_{1g}
1	·	·	·	1	·	T_{1u}
2	·	·	1	·	1	$E_g + T_{2g}$
3	·	1	·	1	1	$A_{2u} + T_{1u} + T_{2u}$
4	1	·	1	1	1	$A_{1g} + E_g + T_{1g} + T_{2g}$
5	·	·	1	2	1	
6	1	1	1	1	2	
7	·	1	1	2	2	
8	1	·	2	2	2	
9	1	1	1	3	2	
10	1	1	2	2	3	
11	·	1	2	3	3	
12	2	1	2	3	3	
13	1	1	2	4	3	
14	1	1	3	3	4	
15	1	2	2	4	4	
16	2	1	3	4	4	
17	1	1	3	5	4	
18	2	2	3	4	5	
19	1	2	3	5	5	
20	2	1	4	5	5	

(5.6.5b)

R(3) characters

$$\chi^{\ell}(\Theta) = \frac{\sin(\ell + \frac{1}{2})\Theta}{\sin\frac{\Theta}{2}}$$

O characters

O	**1**	**r**	$\mathbf{R}^2$	$\mathbf{R}^3$	$\mathbf{i}_k$
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

Frequency of O Irreps

	f^{A_1}	f^{A_2}	f^{E}	f^{T_1}	f^{T_2}	
$l=0$	1	·	·	·	·	A_{1g}
1	·	·	·	1	·	T_{1u}
2	·	·	1	·	1	$E_g + T_{2g}$
3	·	1	·	1	1	$A_{2u} + T_{1u} + T_{2u}$
4	1	·	1	1	1	$A_{1g} + E_g + T_{1g} + T_{2g}$

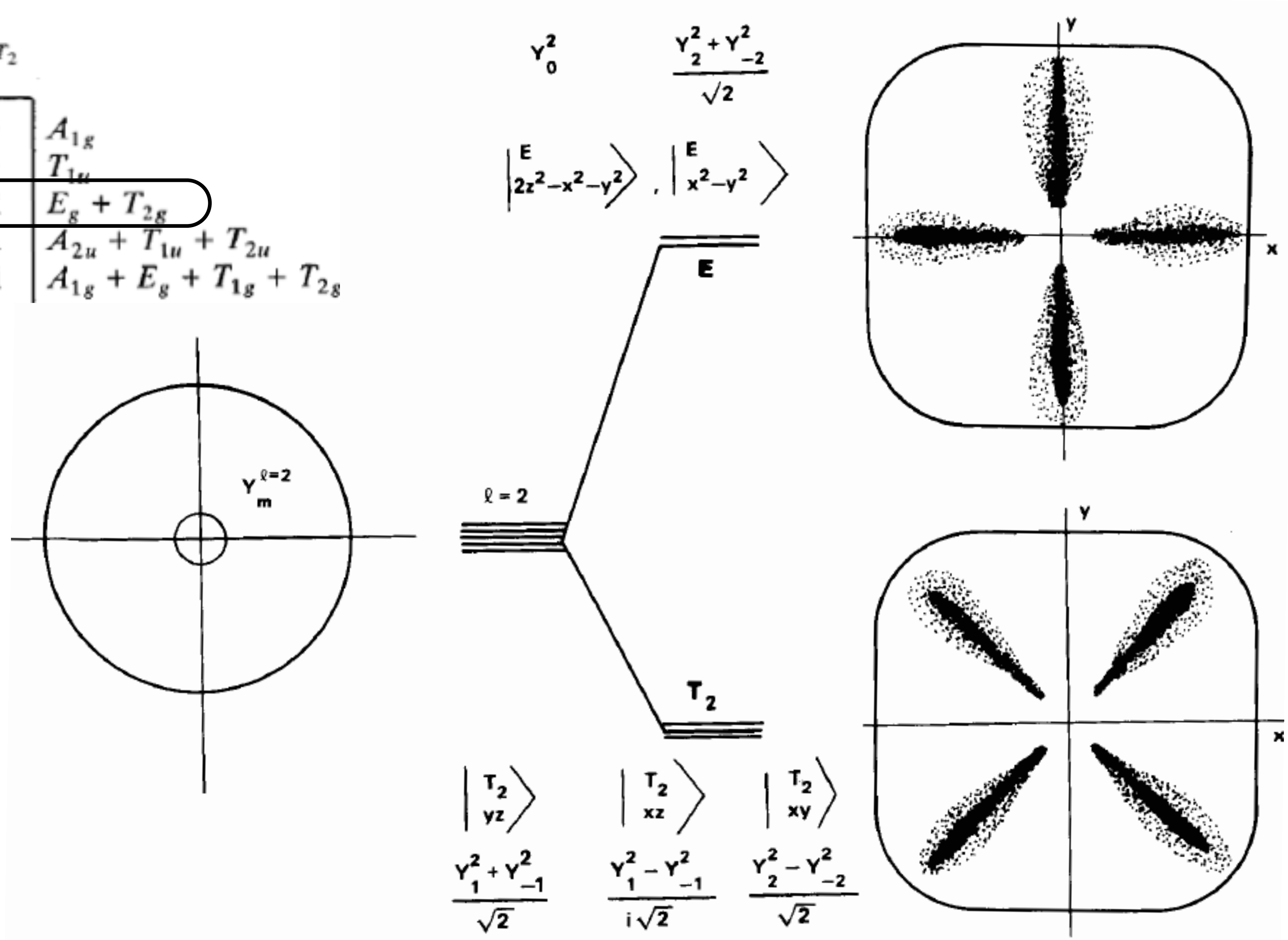


Figure 5.6.3 Detailed sketch of octahedral splitting of a d orbital. The wave functions $\left\langle\left|\begin{smallmatrix}E\\2\end{smallmatrix}\right.\right\rangle$ and $\left\langle\left|\begin{smallmatrix}T_2\\3\end{smallmatrix}\right.\right\rangle$ are sketched inside the equipotential contour $x^4 + y^4 = \text{constant}$ $(z = 0)$.

Review: Spherical rotor levels and RES plots

Spectral fine structure of SF_6, SiF_4, C_8H_8,…

$R(3)\supset O$ symmetry correlation

→ *$O\supset C_4$ 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

From p.6-7 of Lecture 20

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

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

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

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

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

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

Octahedral $O_h \supset O \supset D_4 \supset C_4$ subgroup correlations

From p.6-7 of Lecture 20

$O \downarrow D_4$ subduction

D_4: $\mathbf{1}, \rho_{z180°}, \mathbf{R}_{z\pm 90°}, \rho_{x,y180°}, \mathbf{i}_{3,4}$

$A_1(O)\downarrow D_4 = 1, \quad 1, \quad 1, \quad 1, \quad 1 .$

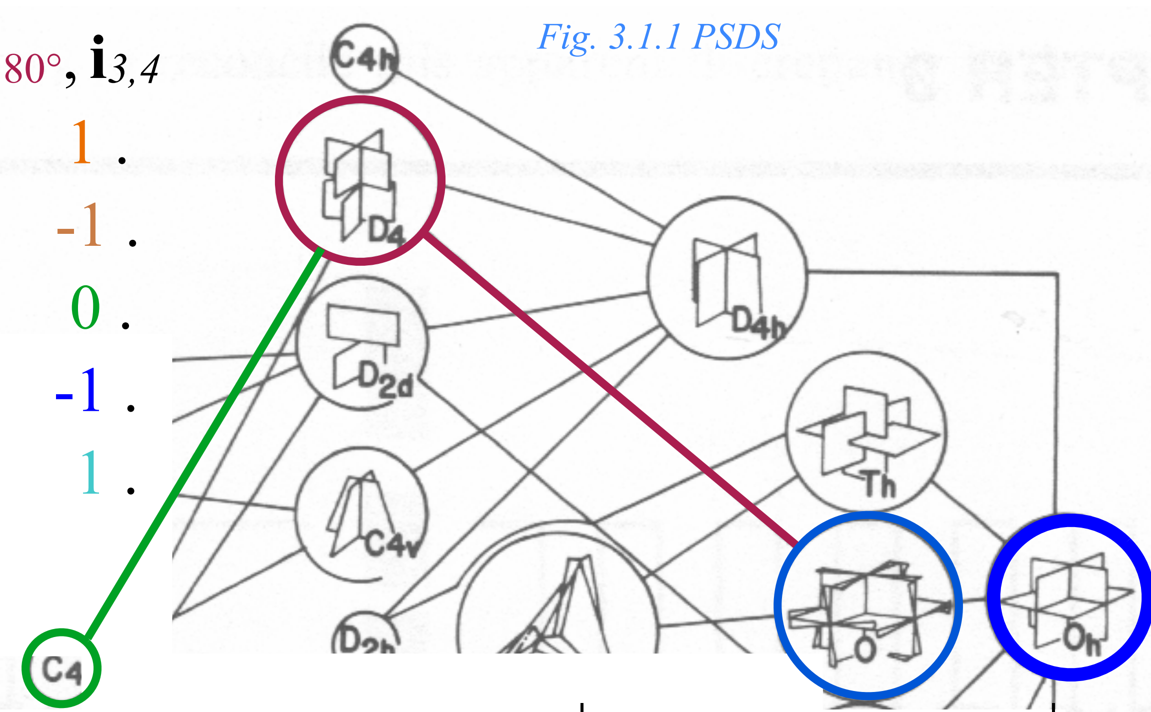
$A_2(O)\downarrow D_4 = 1, \quad 1, \quad -1, \quad 1, \quad -1 .$

$E(O)\downarrow D_4 = 2, \quad 2, \quad 0, \quad 2, \quad 0 .$

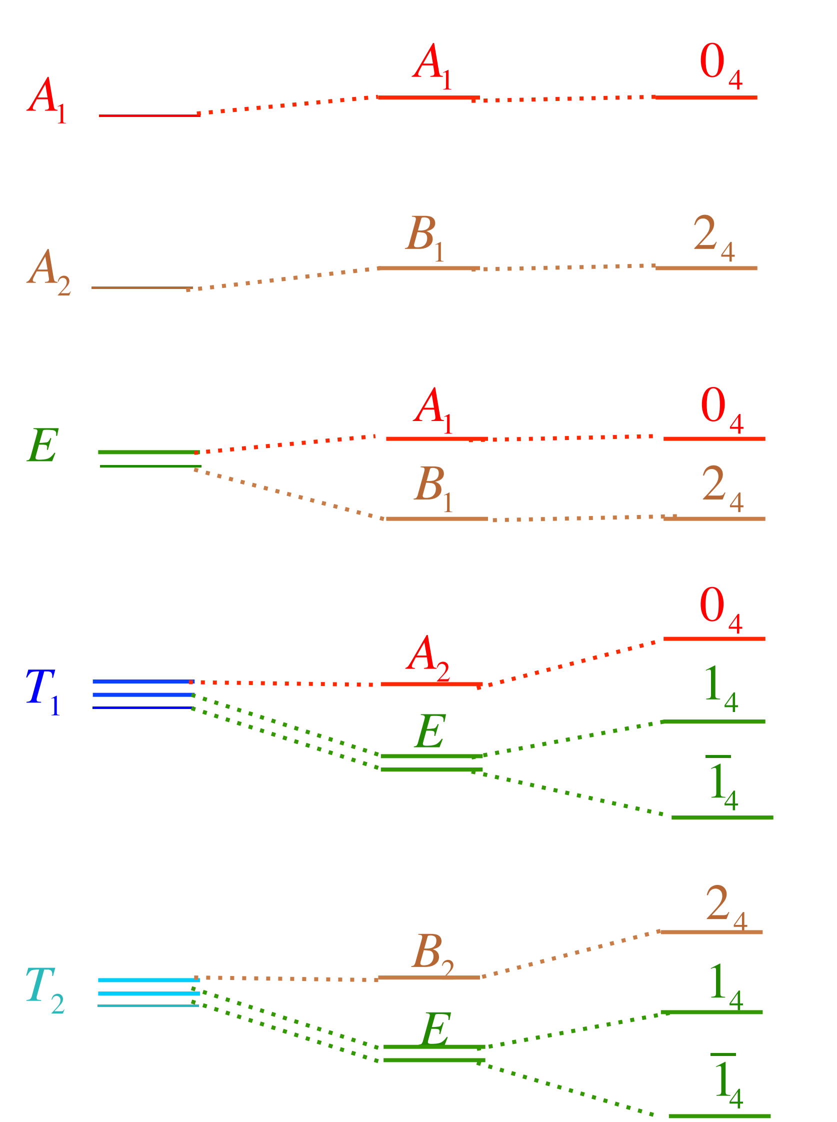
$T_2(O)\downarrow D_4 = 3, \quad -1, \quad 1, \quad -1, \quad -1 .$

$T_2(O)\downarrow D_4 = 3, \quad -1, \quad -1, \quad -1, \quad 1 .$

Fig. 3.1.1 PSDS



$O \supset D_4 \supset C_4$ subgroup and level-splitting/relabeling correlations



$D_4 \downarrow C_4$ subduction

C_4: $\mathbf{1}, \mathbf{R}_{z+90°}, \rho_{z180°}, \mathbf{R}_{z-90°}$

$A_1(D_4)\downarrow C_4 = 1, \quad 1, \quad 1, \quad 1. \quad =(0)_4$

$B_1(D_4)\downarrow C_4 = 1, \quad -1, \quad 1, \quad -1. \quad =(2)_4$

$A_2(D_4)\downarrow C_4 = 1, \quad 1, \quad 1, \quad 1. \quad =(0)_4$

$B_2(D_4)\downarrow C_4 = 1, \quad -1, \quad 1, \quad -1. \quad =(2)_4$

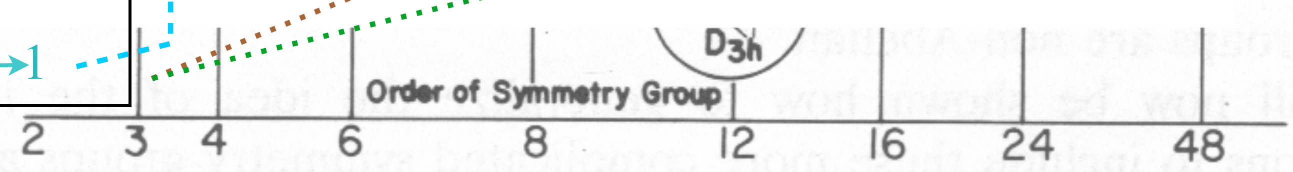
$E(D_4)\downarrow C_4 = 2, \quad 0, \quad -2, \quad 0 . \quad =(1)_4 \oplus (3)_4$

$O \downarrow D_4$	A_1	B_1	A_2	B_2	E
A_1	1	·	·	·	·
A_2	·	1	·	·	·
E	1	1	·	·	·
T_1	·	·	1	·	1
T_2	·	·	·	1	1

$O \downarrow C_4$ 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

$D_4 \downarrow C_4$	0_4	1_4	2_4	$3_4 = \bar{1}_4$
A_1	1	·	·	·
B_1	·	·	1	·
A_2	1	·	·	·
B_2	·	·	→1	·
E	·	→1	·	→1



$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

$(A_1\ T_1\ E)_{0_4}\ (T_2\ T_1)_{3_4}\ (E\ T_2\ A_2)_{2_4}\ (T_2\ T_1)_{1_4} \ldots (A_2\ T_2\ T_1\ A_1)_{0_3}\ (T_1\ E\ T_2)_{1_3}\ (T_1\ E\ T_2)_{2_3} \ldots$

Bands or "Clusters" of levels maintain order but change spacing as they adapt to varying local symmetries by crossing separatrices in their phase space (see p. 73-77)

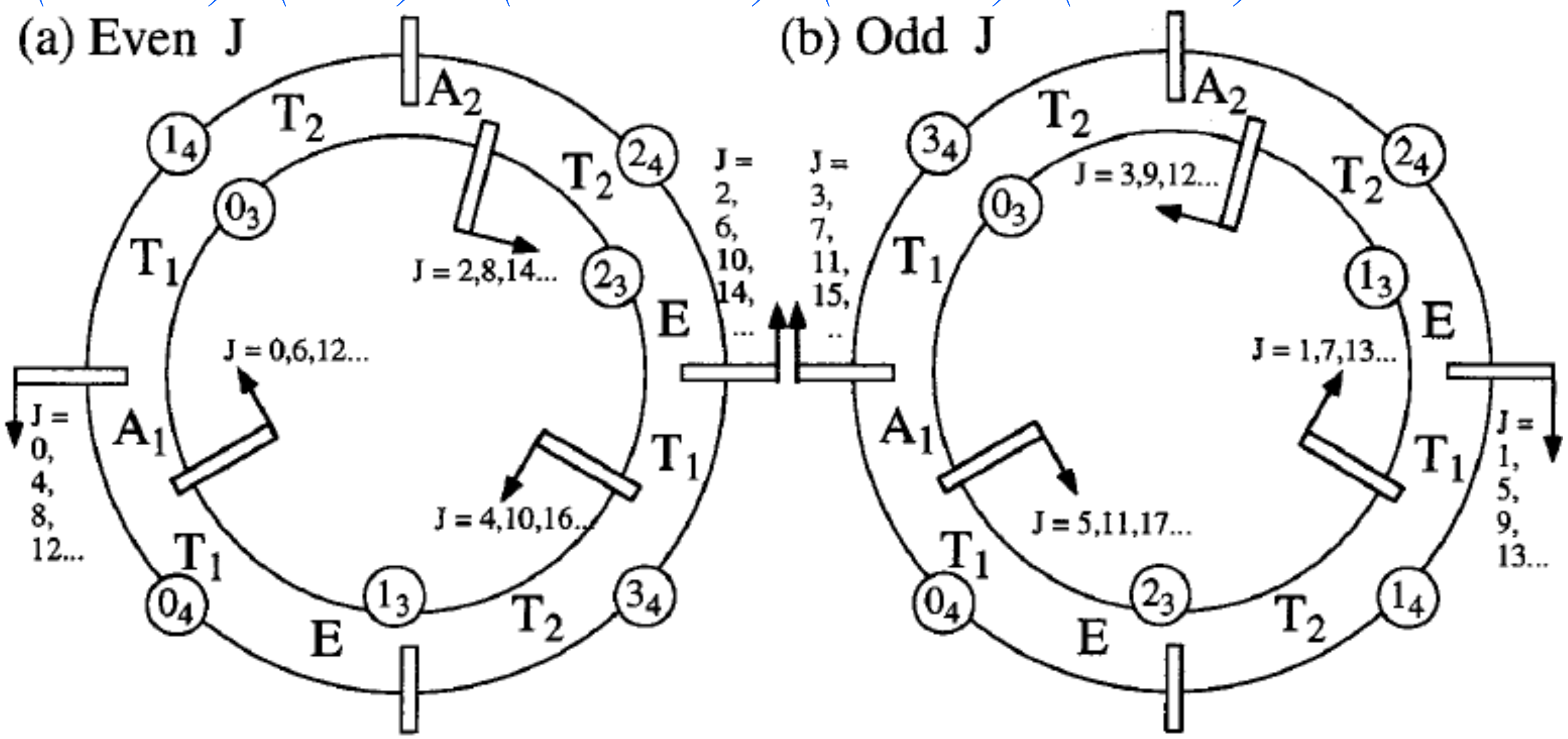


Figure 5.6.9 Mnemonic wheels for octahedral-O orbital. Splitting of J levels for (a) even J and (b) odd J.

$R(3) \subset O(3) \supset O_h \supset O$ character analysis (From Principles of Symmetry Dynamics & Spectroscopy Ch.5 p.403)

$(A_1\ T_1\ E)_{0_4}\ (T_2\ T_1)_{3_4}\ (E\ T_2\ A_2)_{2_4}\ (T_2\ T_1)_{1_4} \ldots (A_2\ T_2\ T_1\ A_1)_{0_3}\ (T_1\ E\ T_2)_{1_3}\ (T_1\ E\ T_2)_{2_3} \ldots$

Bands or "Clusters" of levels maintain order but change spacing as they adapt to varying local symmetries by crossing separatrices in their phase space (see p. 73-77)

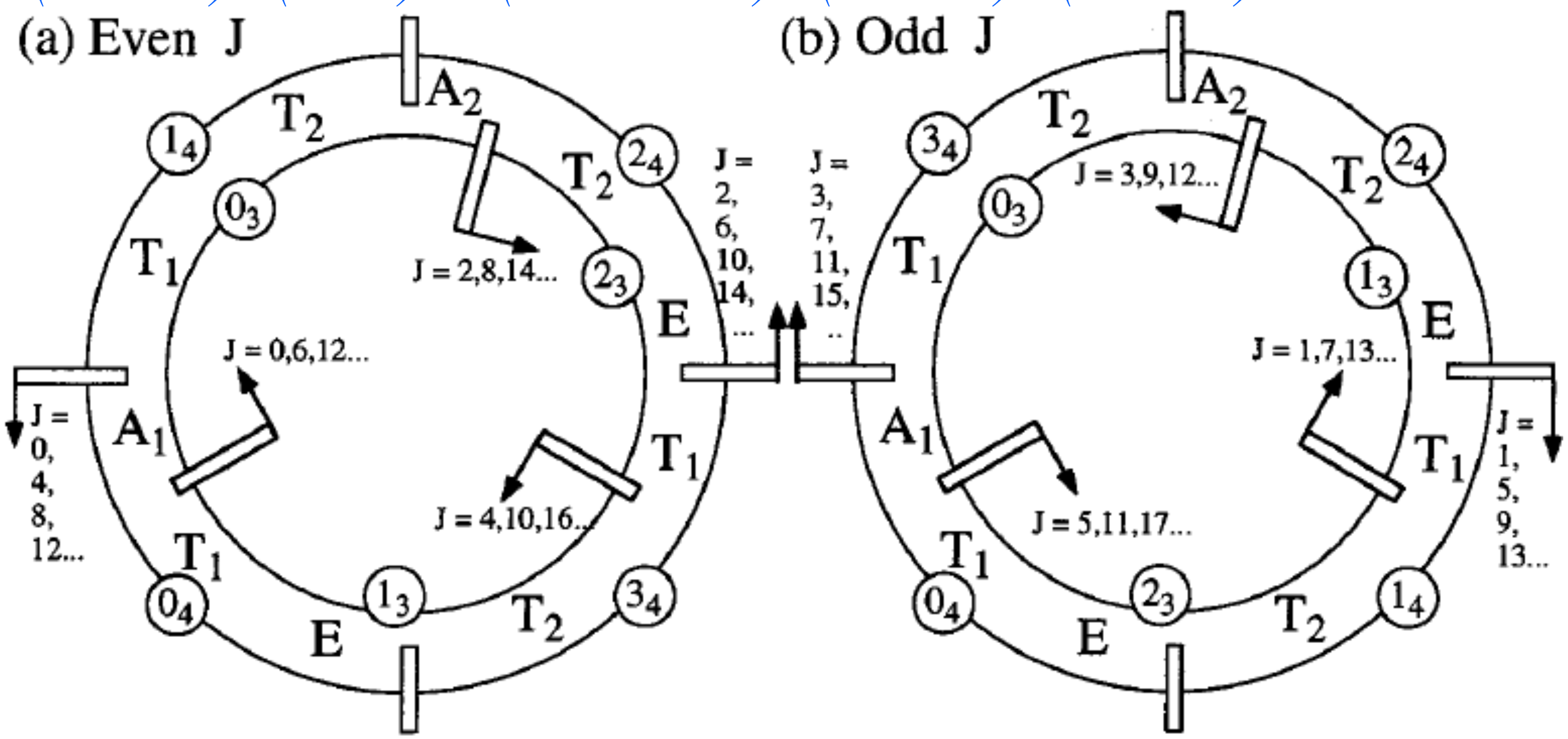
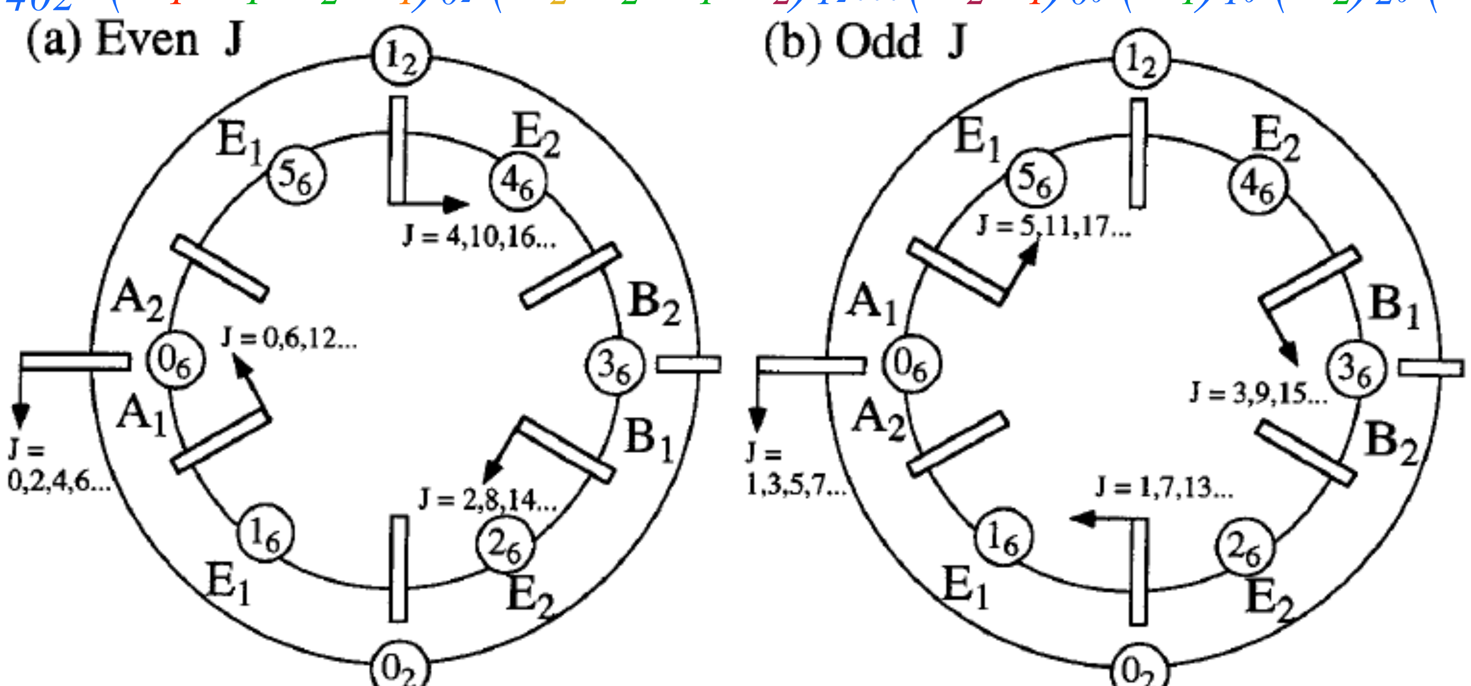


Figure 5.6.9 Mnemonic wheels for octahedral-*O* orbital. Splitting of *J* levels for (a) even *J* and (b) odd *J*.

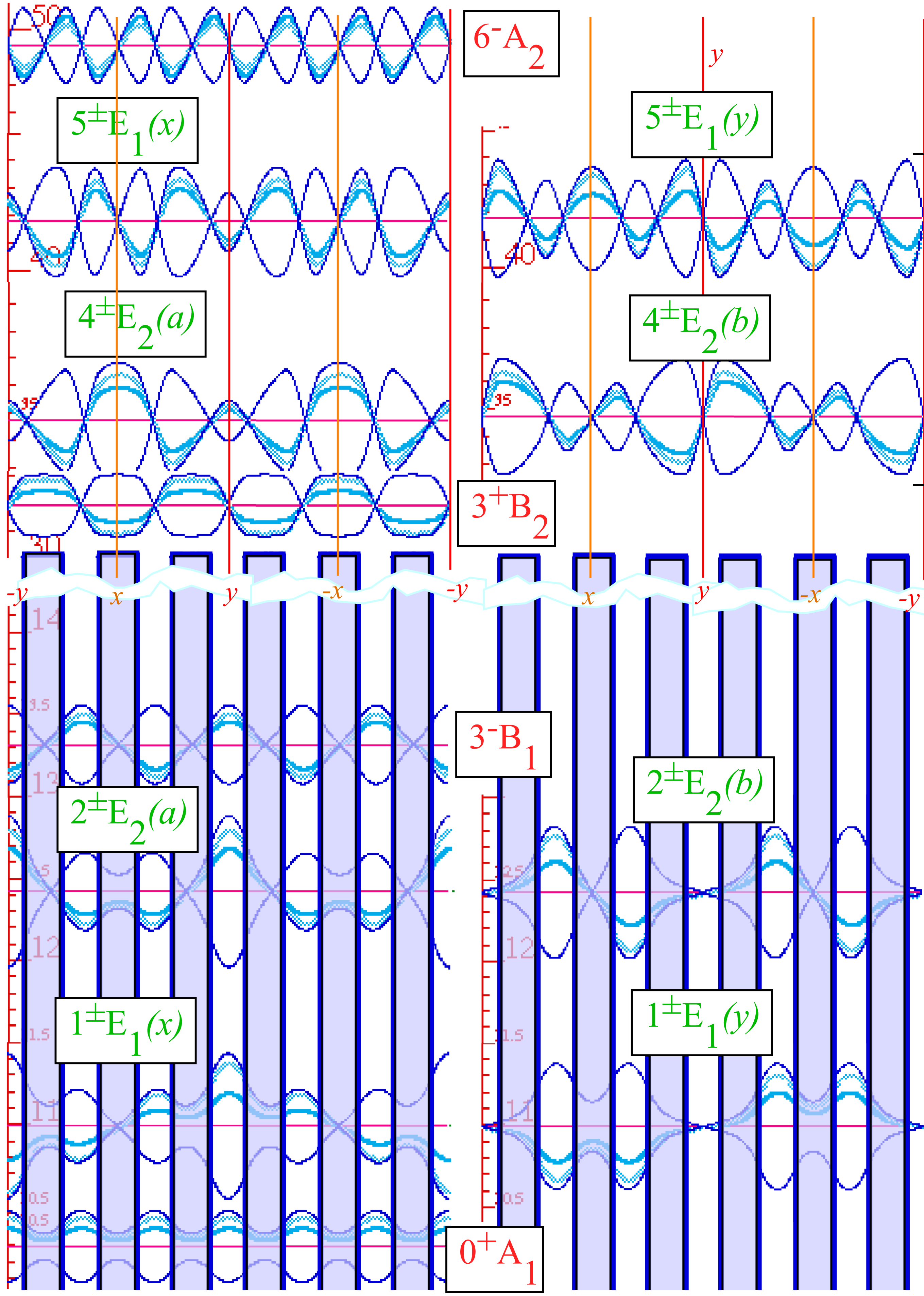
D_6 wheel

Ch.5 p.402 $(A_1\ E_1\ E_2\ B_1)_{0_2}\ (B_2\ E_2\ E_1\ A_2)_{1_2} \ldots (A_2 A_1)_{0_6}\ (E_1)_{1_6}\ (E_2)_{2_6}\ (B_1\ B_2)_{3_6} (E_2)_{4_6}\ (E_1)_{5_6} \ldots$



(see p. 68-72 of Lect. 18 where "band" and "gap" spacing varies with energy)

D_6 Band structure and related induced representations (Mac OS-9)



$D_6 \supset C_3(h)$	0_6	1_6	2_6	3_6	4_6	5_6
A_1	1	·	·	·	·	·
A_2	1	·	·	·	·	·
E_2	·	·	1	·	1	·
B_2	·	·	·	1	·	·
B_1	·	·	·	1	·	·
E_1	·	1	·	·	·	1

$1_2 \uparrow D_3 \sim A_2 \oplus E_2 \oplus E_1 \oplus B_2$

Odd Band or Cluster

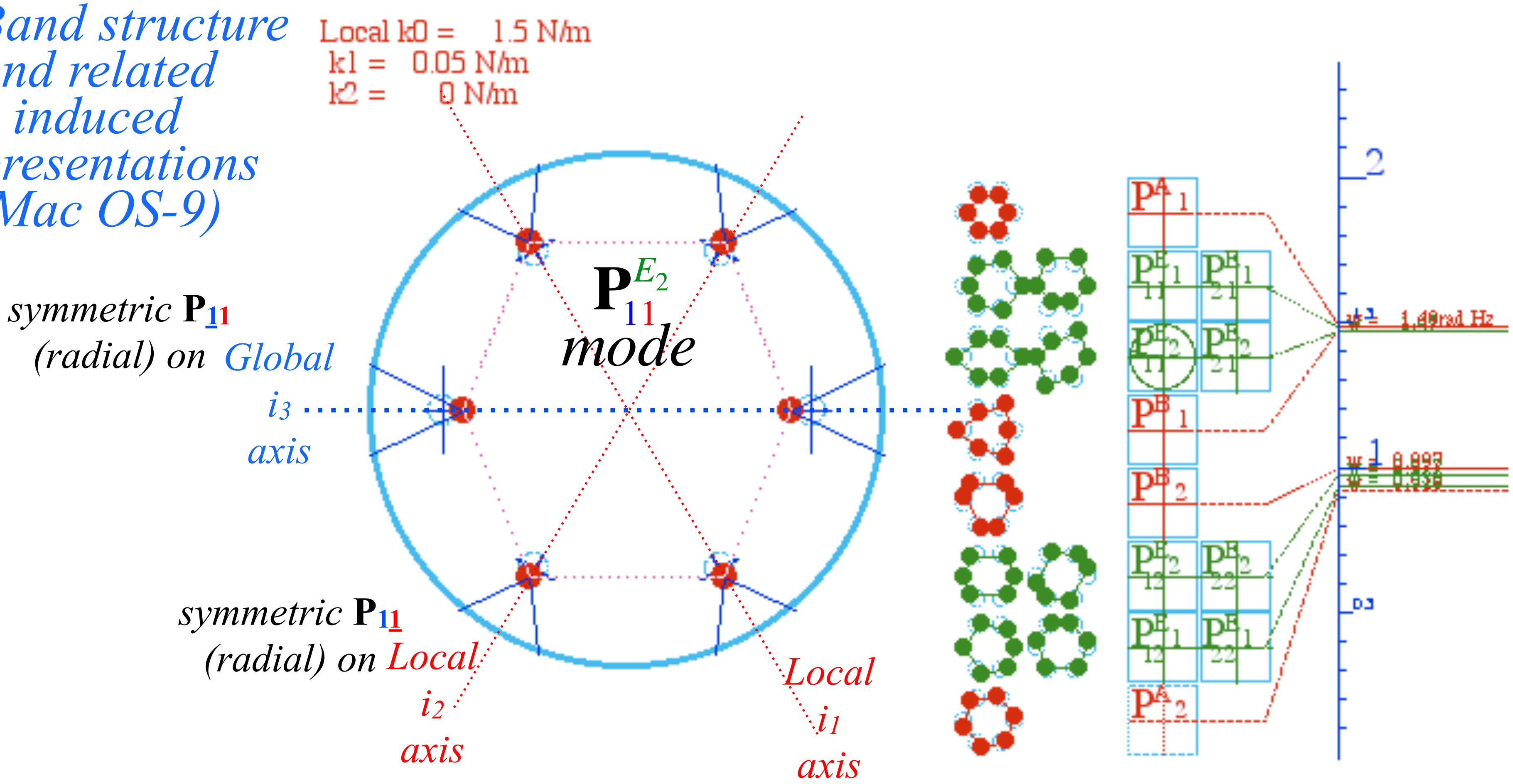
$0_2 \uparrow D_3 \sim A_1 \oplus E_1 \oplus E_2 \oplus B_1$

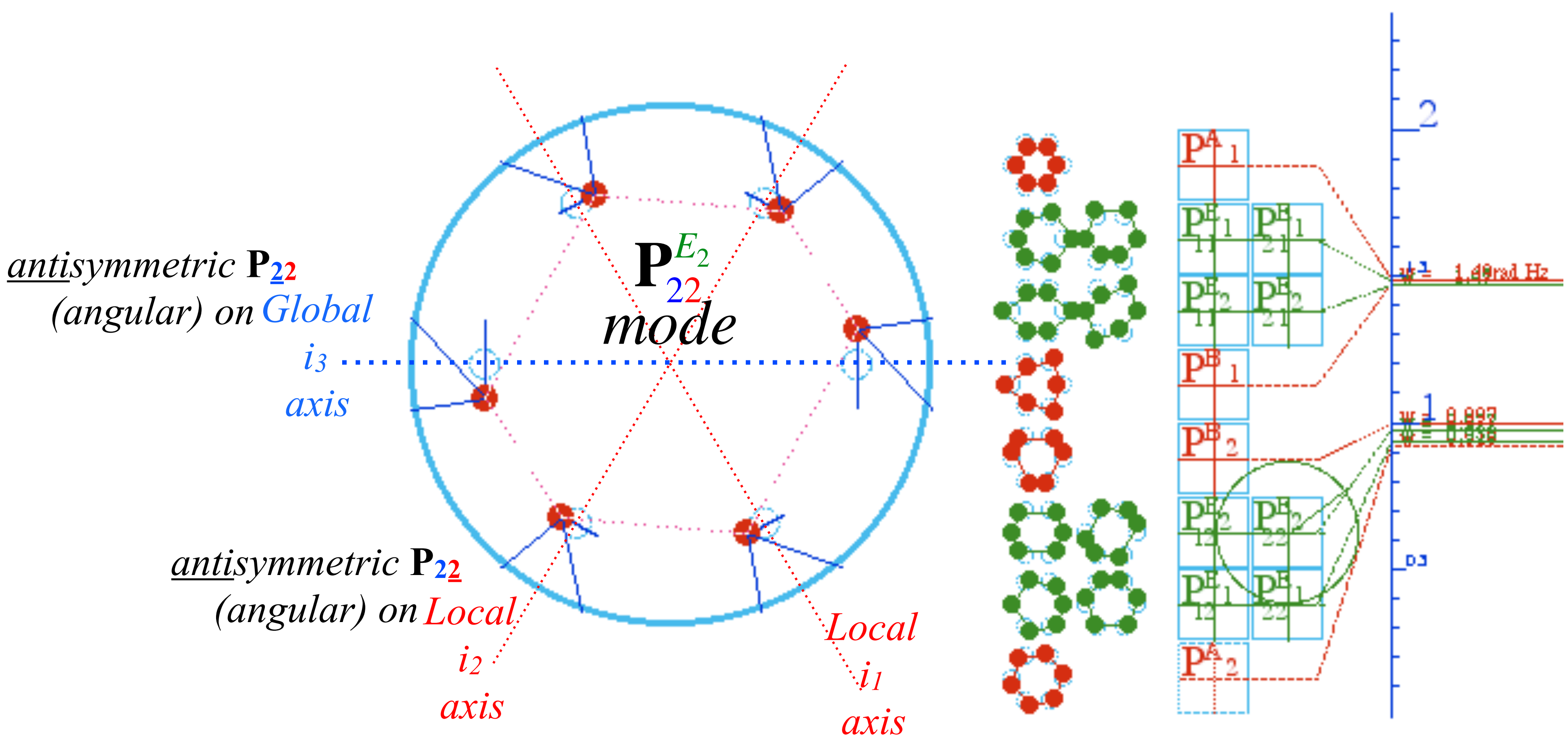
Even Band or Cluster

$D_3 \supset C_2(j_3)$	0_2	1_2
A_1	1	·
A_2	·	1
E_2	1	1
B_2	·	1
B_1	1	·
E_1	1	1

(p. 68 of Lect. 18)

D_6 Band structure and related induced representations (Mac OS-9)





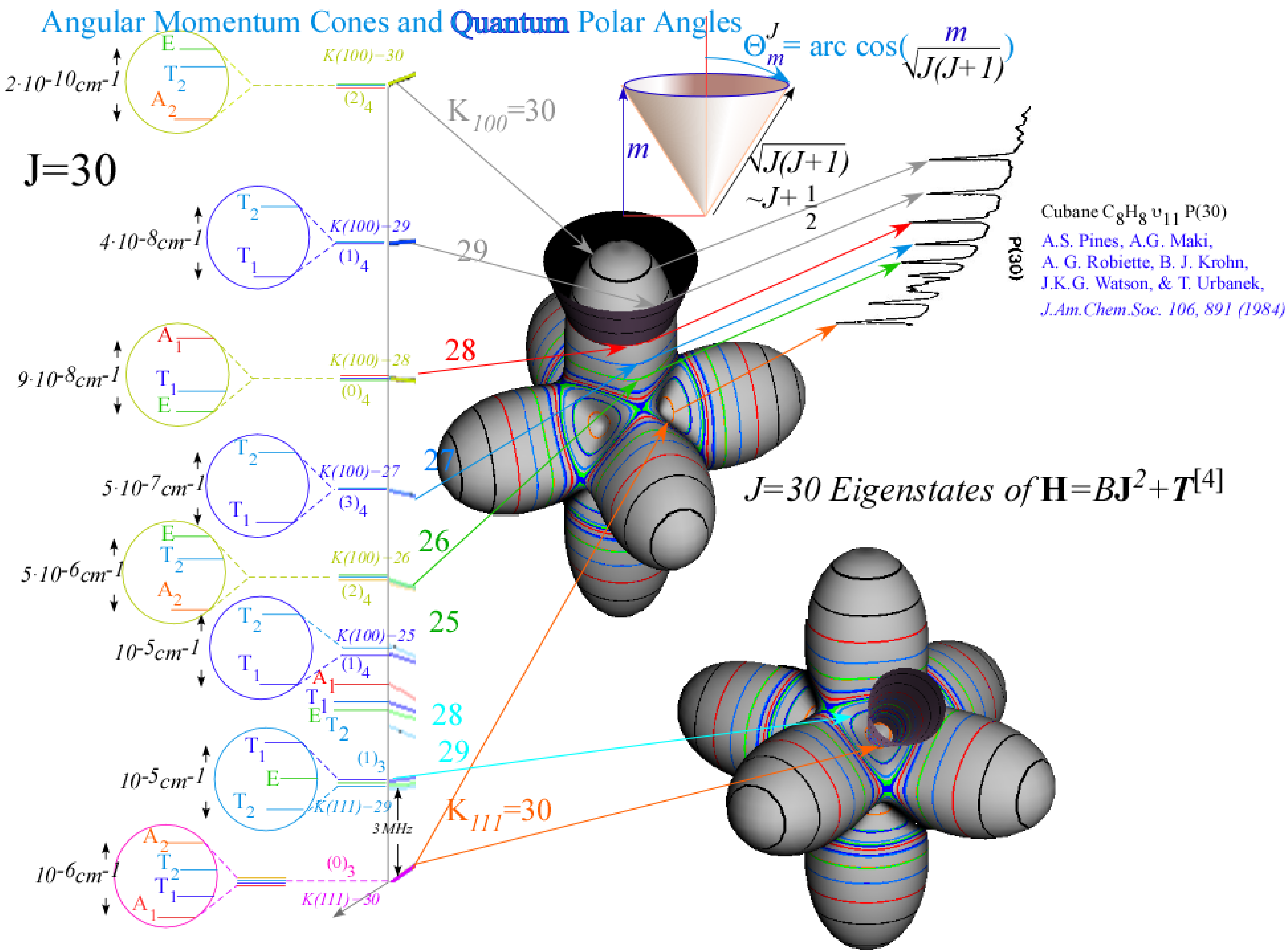
(p. 69 of Lect. 18)

Review: *Spherical rotor levels and RES plots*

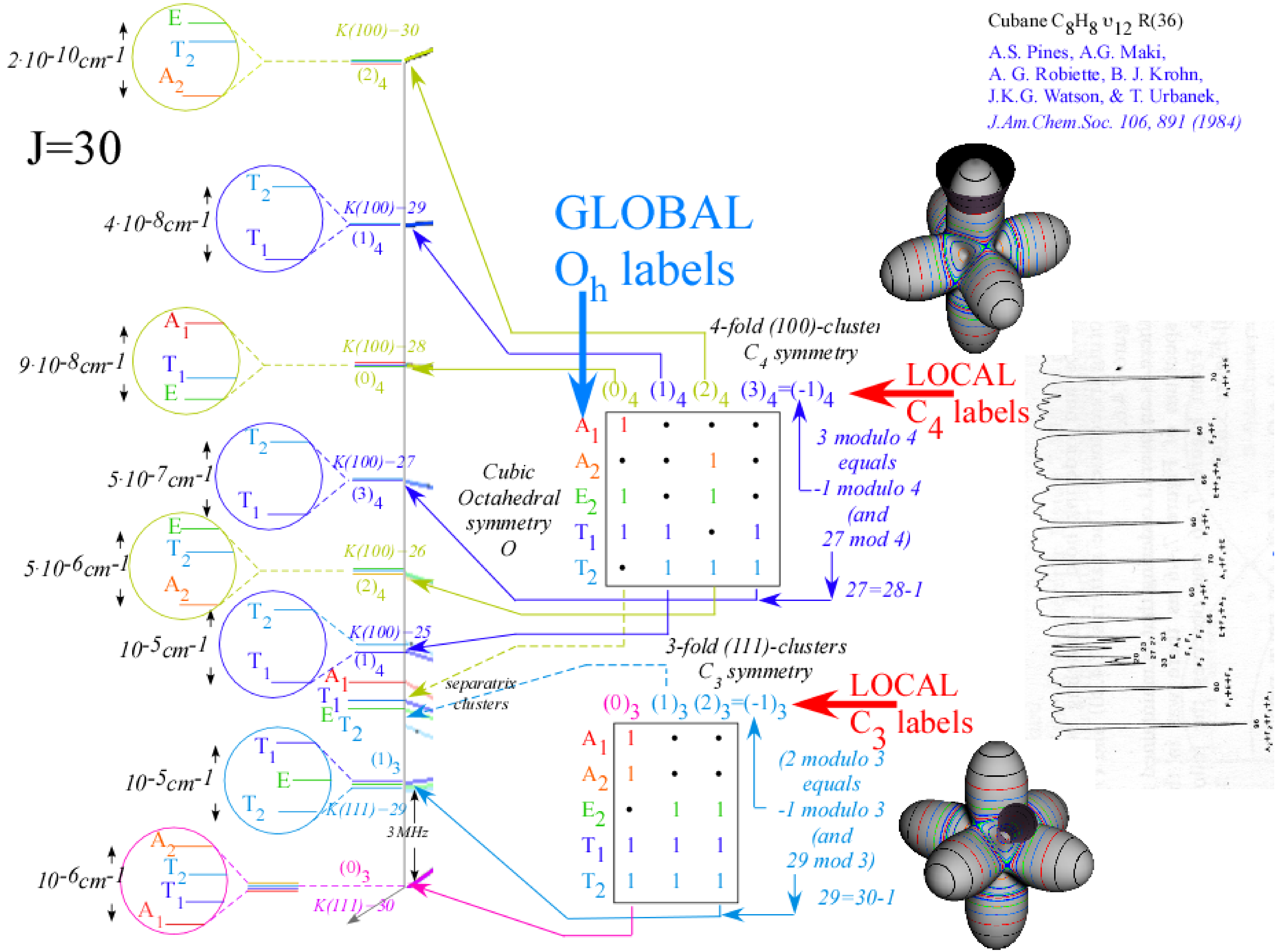
Spectral fine structure of SF_6, SiF_4, C_8H_8,...

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

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

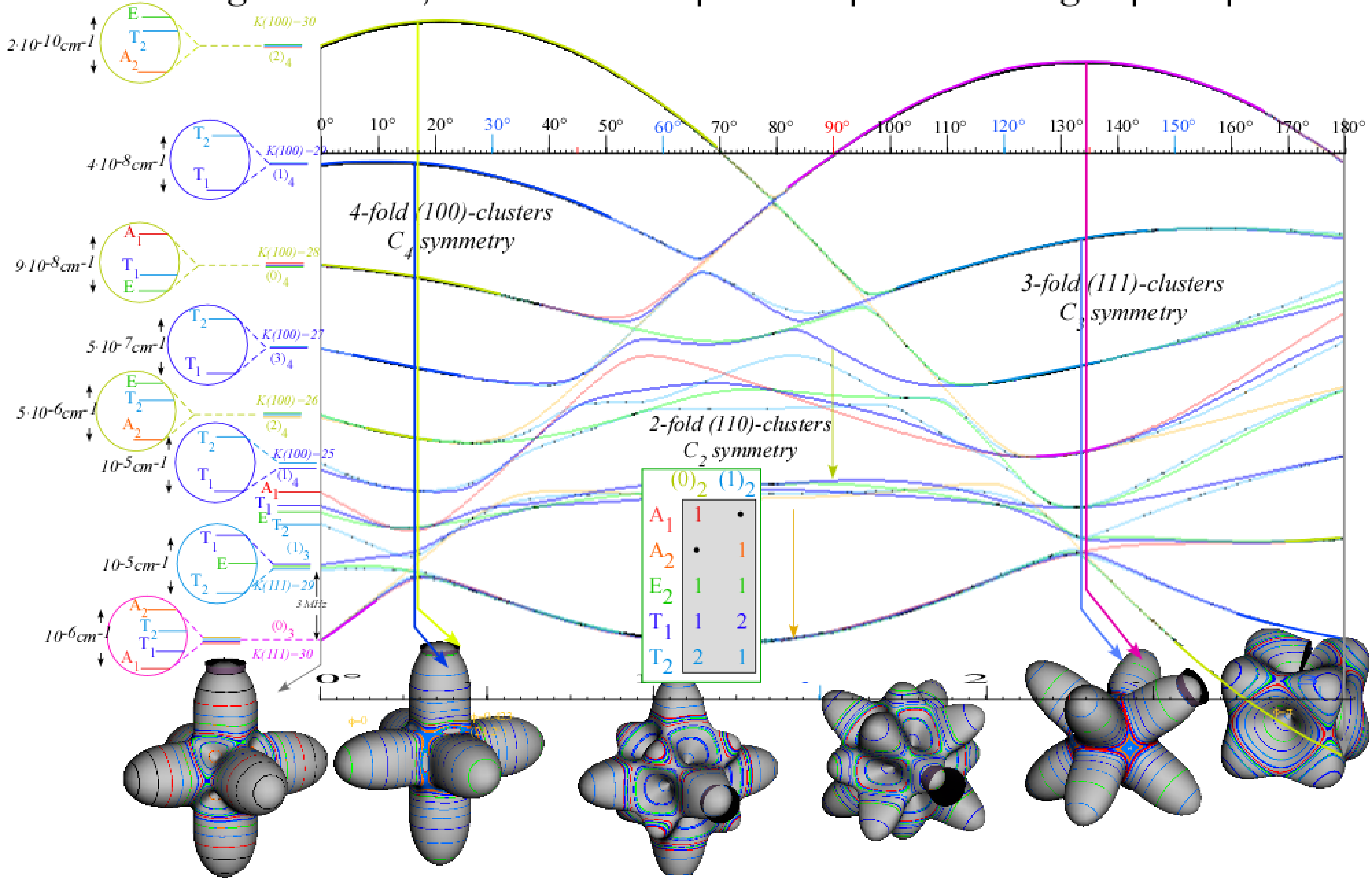

Angular Momentum Cones and Quantum Polar Angles
$\Theta_m^J = \arccos\left(\frac{m}{\sqrt{J(J+1)}}\right)$
m
$\sqrt{J(J+1)}$
$\sim J+\frac{1}{2}$
J=30
$2\cdot10^{-10}cm^{-1}$
$4\cdot10^{-8}cm^{-1}$
$9\cdot10^{-8}cm^{-1}$
$5\cdot10^{-7}cm^{-1}$
$5\cdot10^{-6}cm^{-1}$
$10^{-5}cm^{-1}$
$10^{-5}cm^{-1}$
$10^{-6}cm^{-1}$
K(100)=30
K(100)=29
K(100)=28
K(100)=27
K(100)=26
K(100)=25
K(111)=29
K(111)=30
$(2)_4$
$(1)_4$
$(0)_4$
$(3)_4$
$(2)_4$
$(1)_4$
$(1)_3$
$(0)_3$
3 MHz
K_{100}=30
29
28
27
26
25
28
29
K_{111}=30
P(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



J=30 multiplet variation due to adding $\mathbf{T}^{[6]}$ *to* $\mathbf{T}^{[4]}$

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



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(54) 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.

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
	$\nu_3/2\nu_4$

Details of P(88) v_4 SF_6 and P(54) 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

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OUTLINE

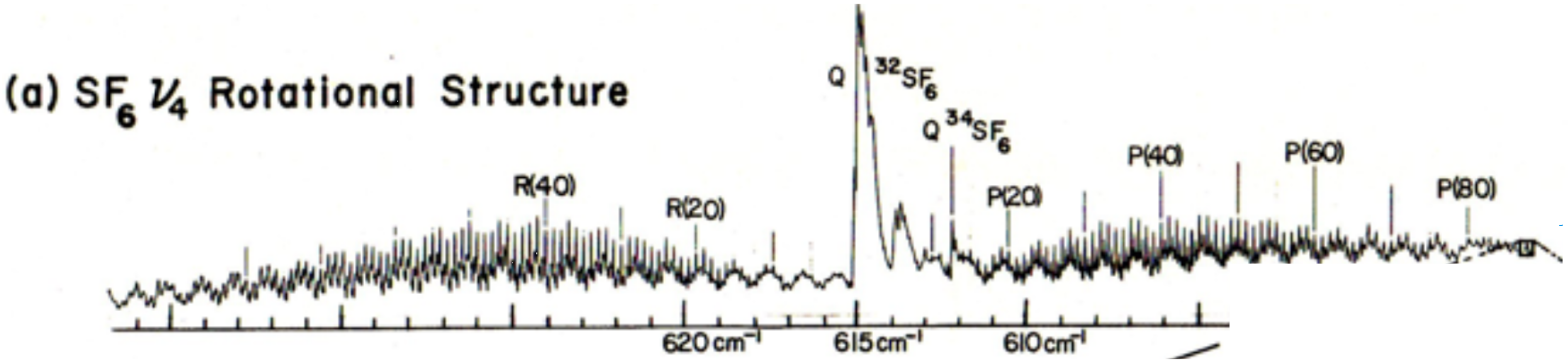
Introductory review — Example(s)

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

Recent developments

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

Gyro-rotor & Born-Oppenheimer theory starts on p. 19 of Lecture 28



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*

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

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

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

Involves:

angular momentum ℓ of vibration "orbits"

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

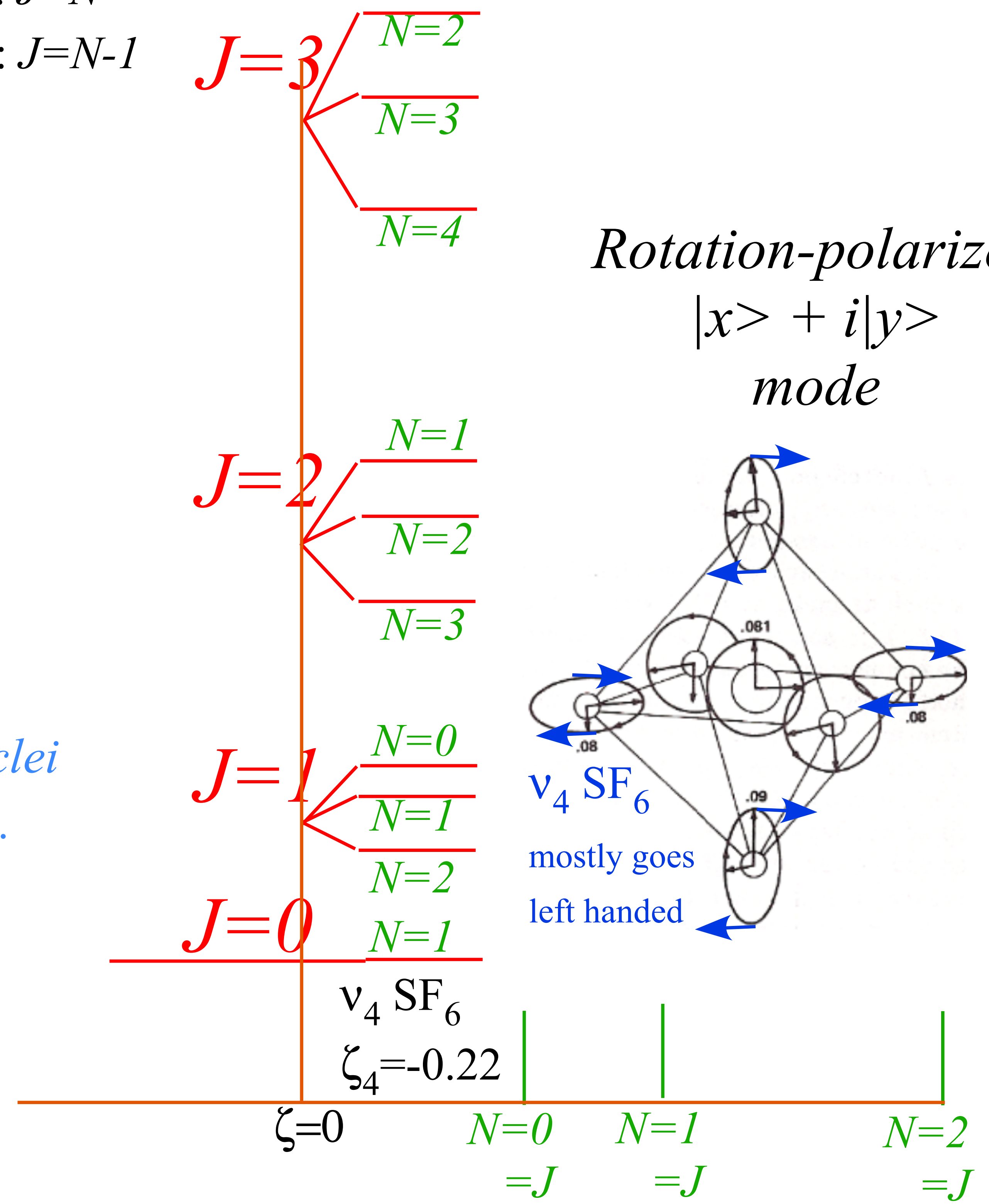
total momentum **J** $=\ell+\mathbf{N}$ *of whole molecule.*

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

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

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

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

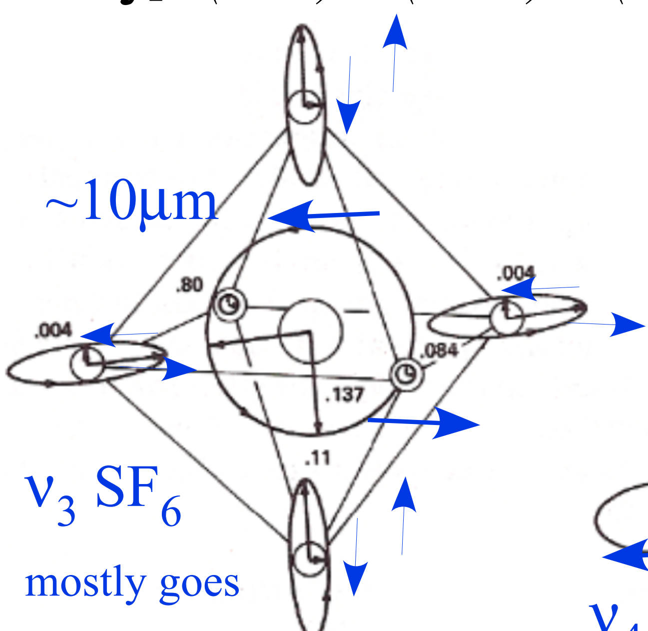


$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

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

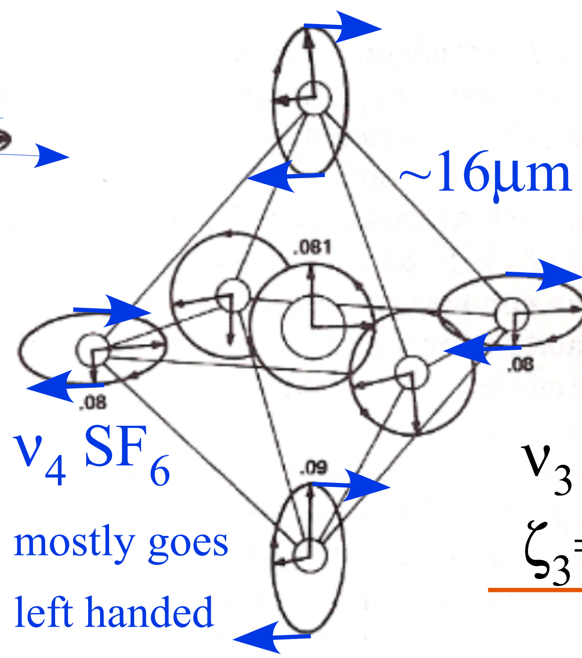
$$\begin{aligned} H^{Scalar\ Coriolis} &= -B\zeta\, 2\mathbf{J}^{Total}\bullet\ell^{vibe} \\ &= -B\zeta\,[\,\mathbf{J}^2-(\mathbf{J}-\ell)^2+\ell^2] \\ &= -B\zeta\,[\,\mathbf{J}^2-\ \mathbf{N}^2\ +\ell^2] \end{aligned}$$

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



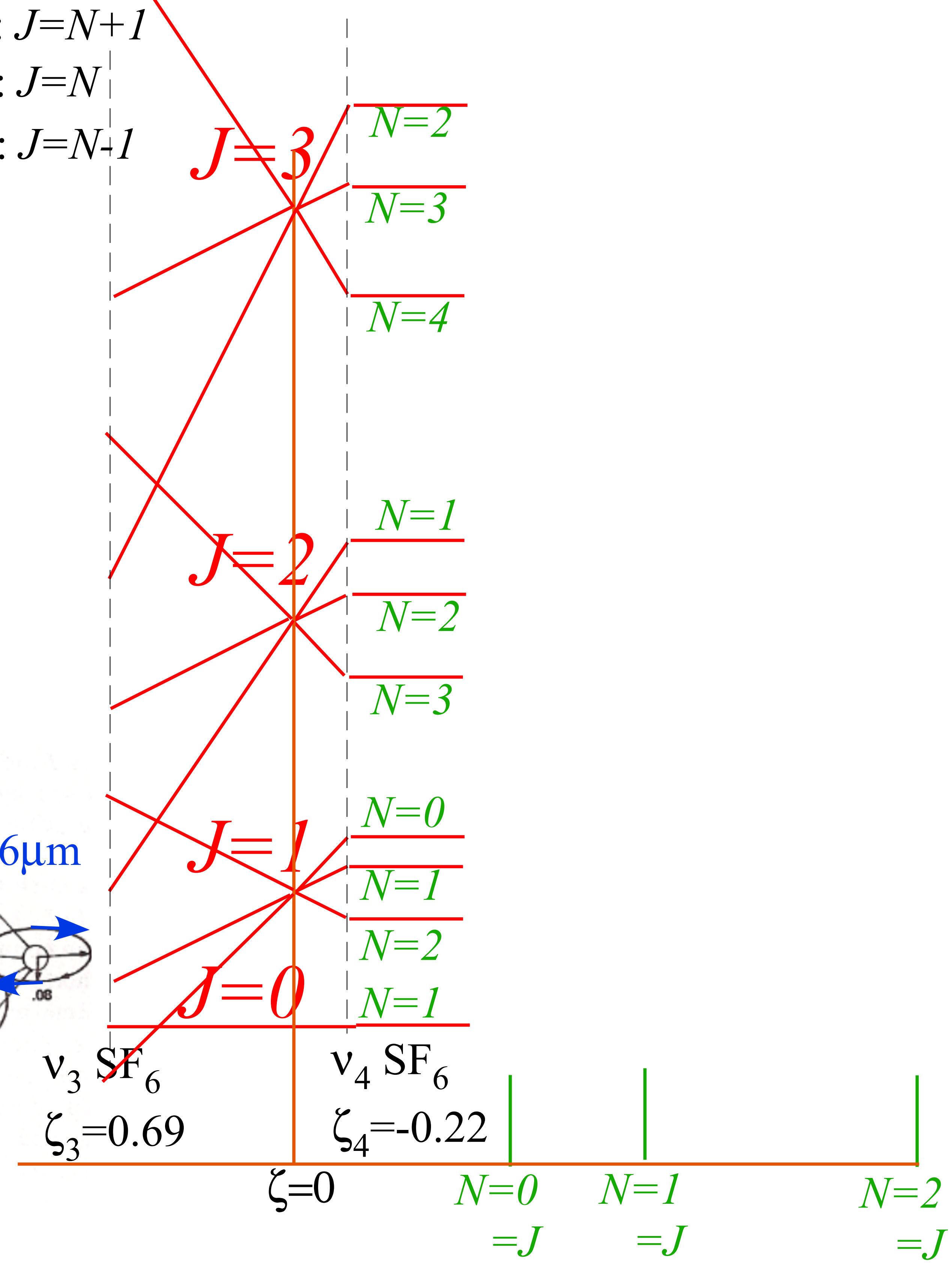
ν_3 SF_6

mostly goes right handed



ν_4 SF_6

mostly goes left handed



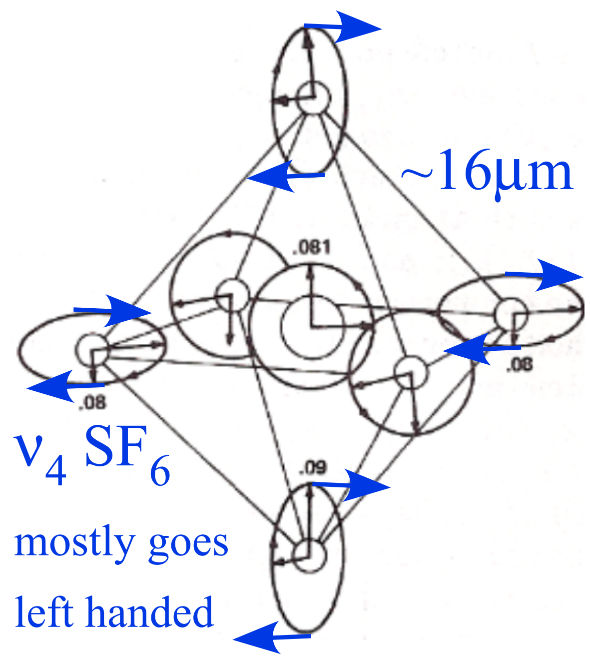
Details of P(88) v_4 SF_6 and P(54) v_4 CF_4 spectral structure and implications

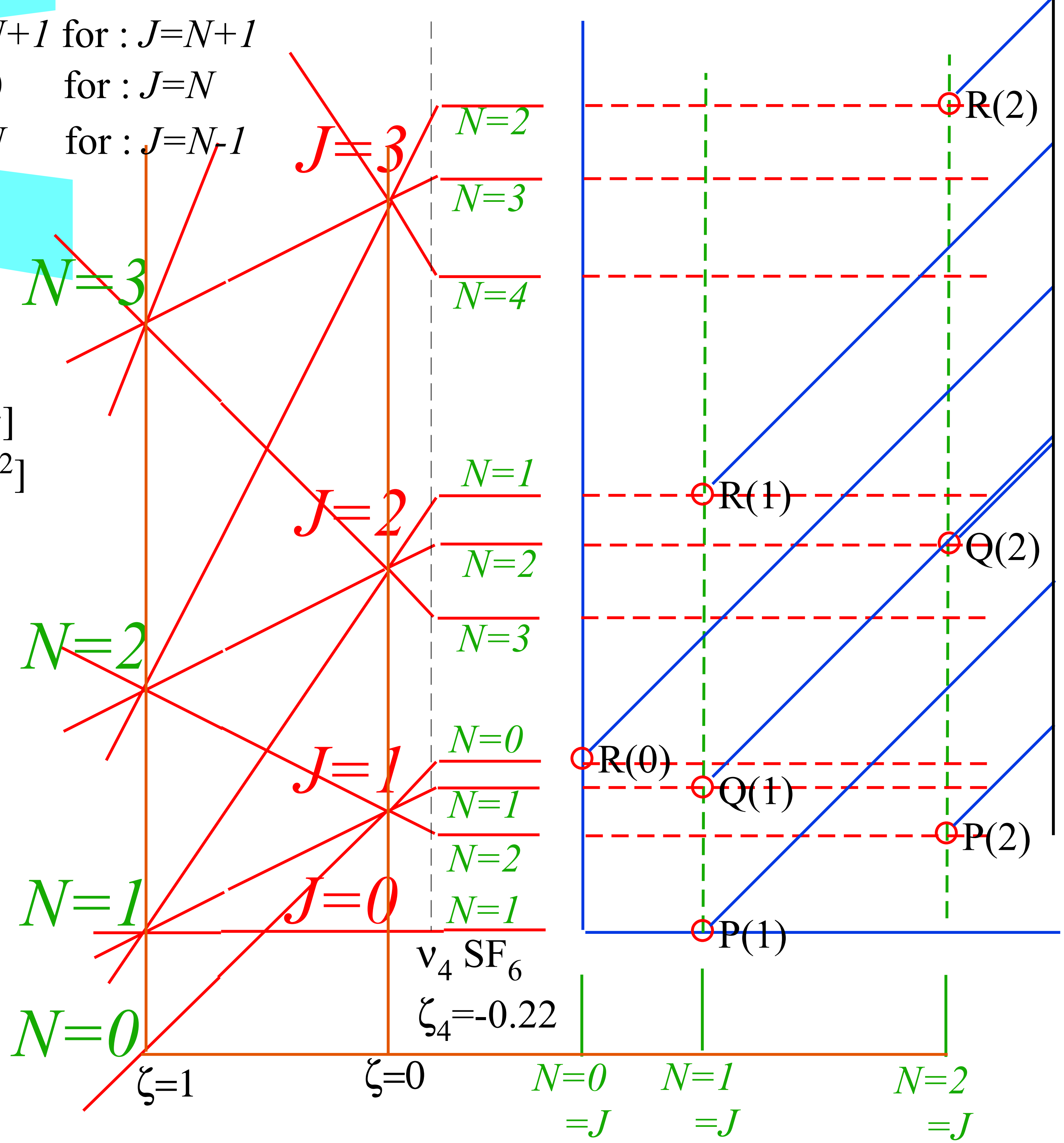
- *Outline of rovibronic Hamiltonian theory*
    - *Coriolis scalar interaction*
- *Rovibronic nomograms and PQR structure*
- *Rovibronic energy surfaces (RES) and cone geometry*
- *Spin symmetry correlation, tunneling, and entanglement*
    - *Hyperfine vs. superfine structure (Case 1. vs Case 2.)*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

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

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

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

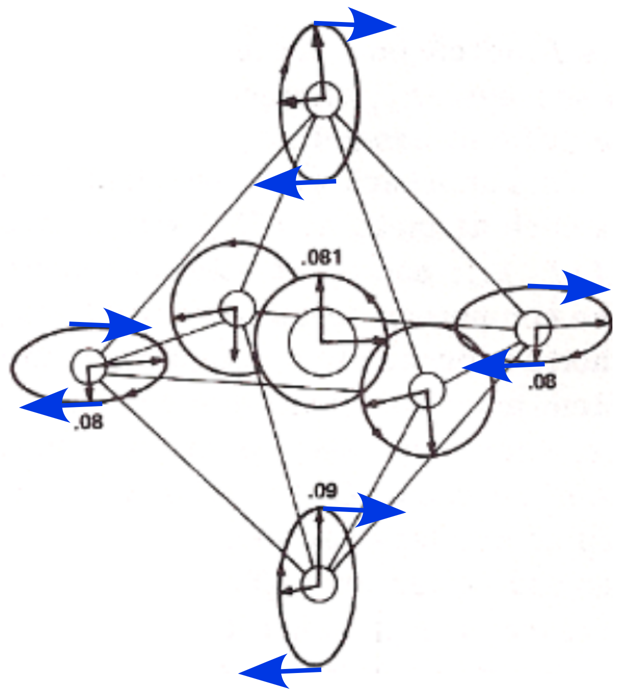


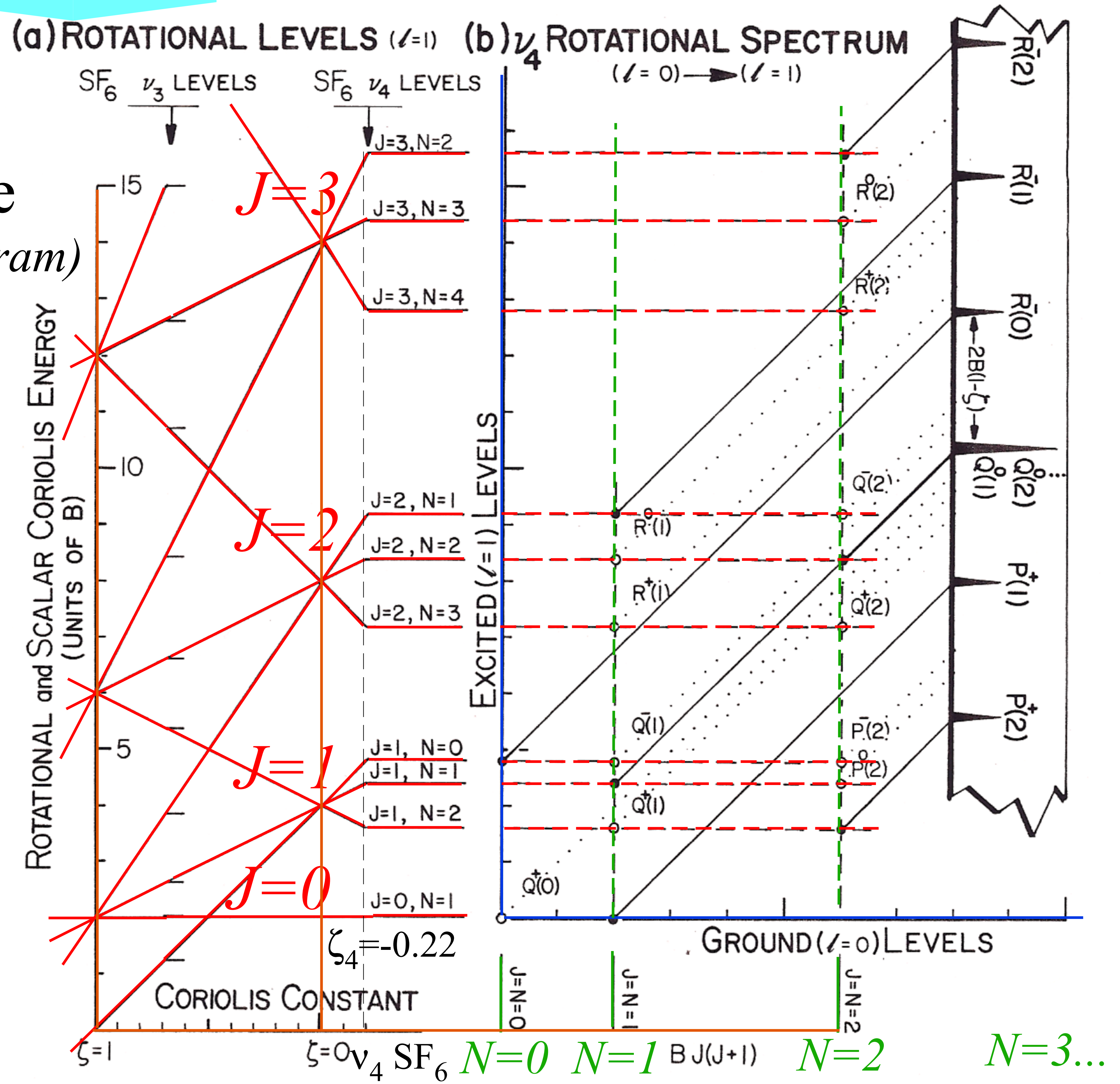


$$\langle H \rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis} \rangle + \langle H^{Tensor\ Centrifugal} \rangle + \langle H^{Tensor\ Coriolis} \rangle + \langle H^{Nuclear\ Spin} \rangle + \ldots$$

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

(Using rovib. nomogram)





Details of P(88) ν_4 SF_6 and P(54) ν_4 CF_4 spectral structure and implications

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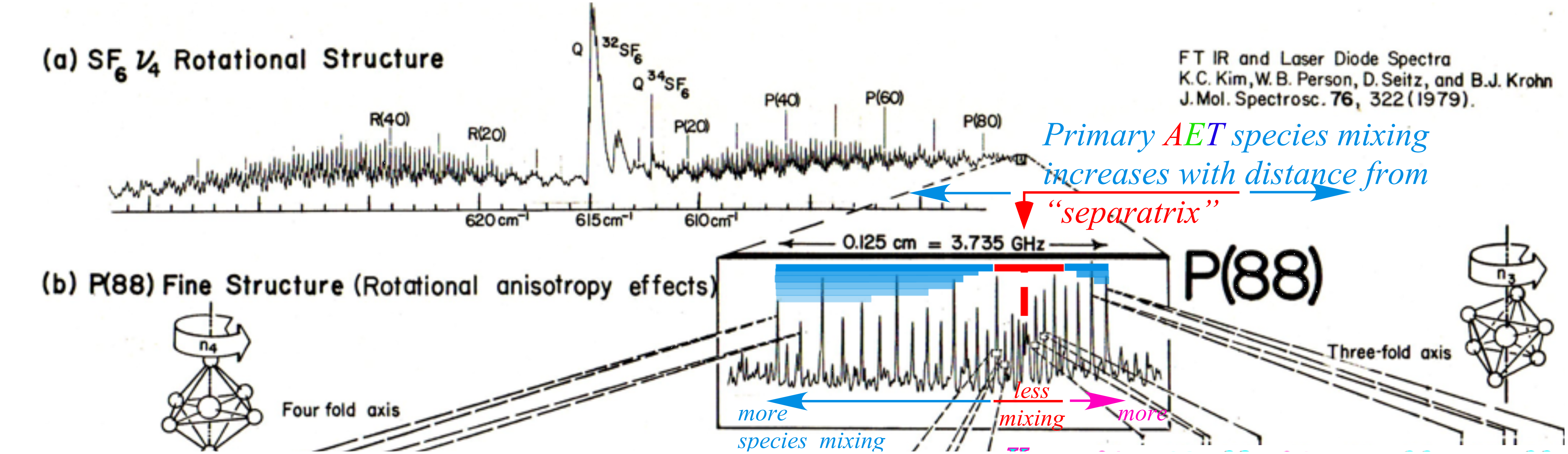


PQR structure due to Coriolis scalar interaction between vibrational angular momentum ℓ and total momentum $\mathbf{J} = \ell + \mathbf{N}$ of rotating nuclei

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

Graphical approach to rotation-vibration-spin Hamiltonian

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

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

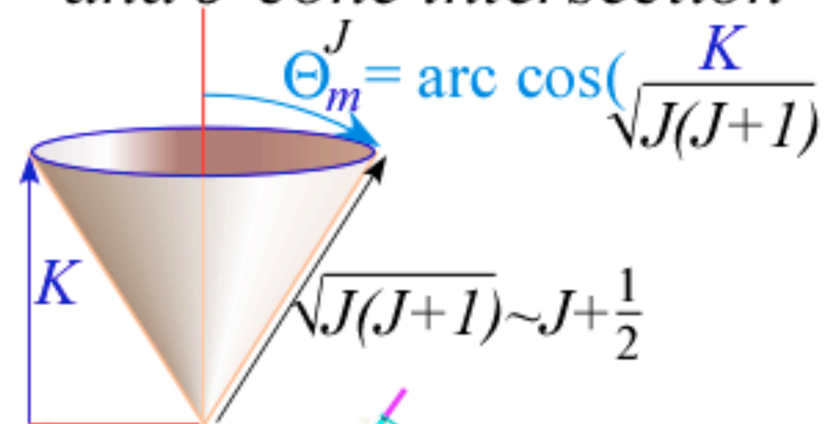
Recent developments

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

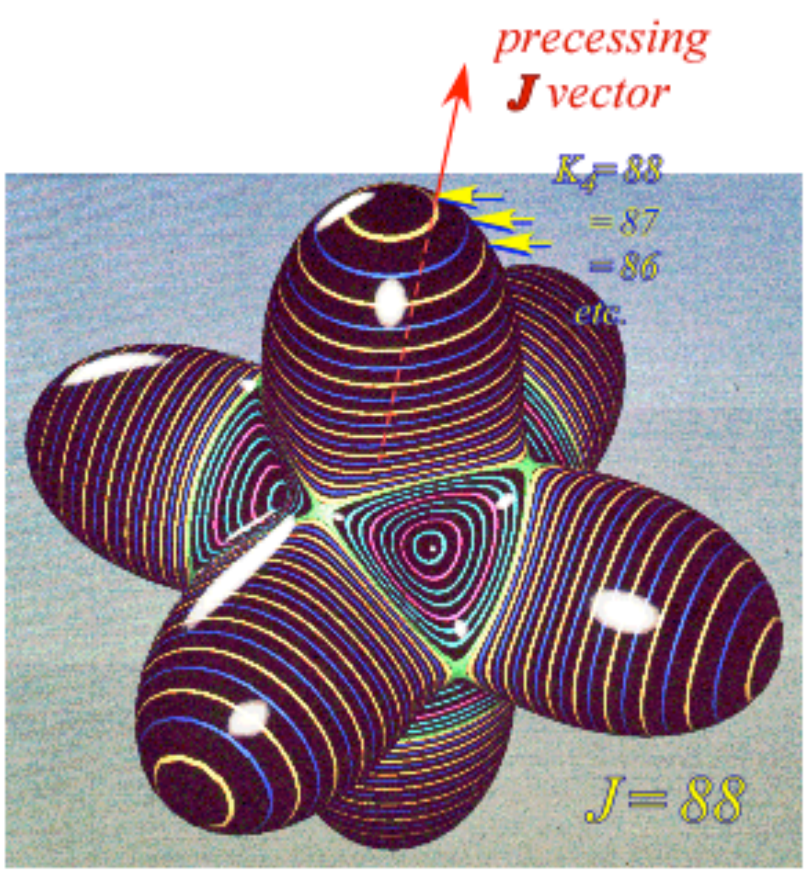
SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography and J-cone intersection

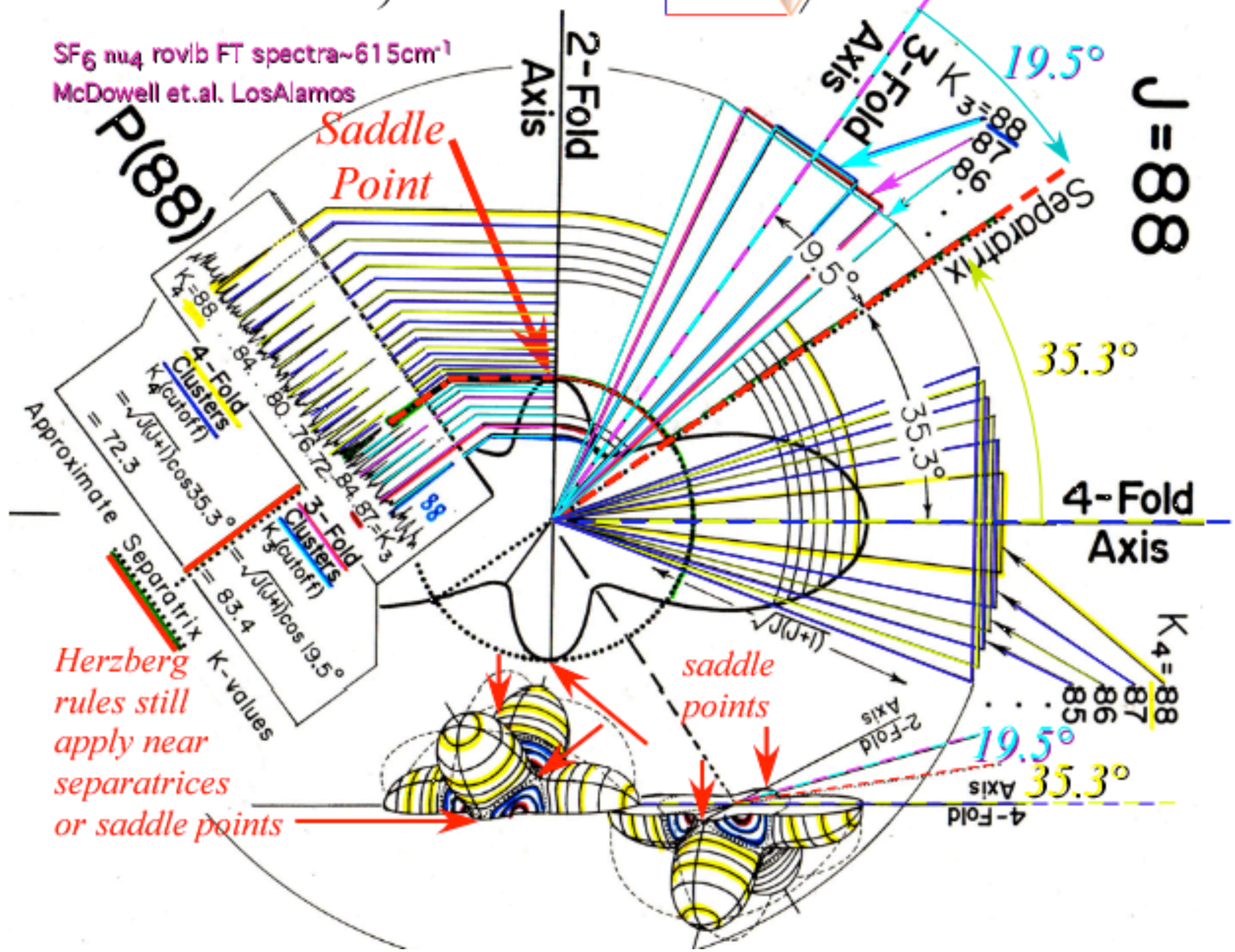
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

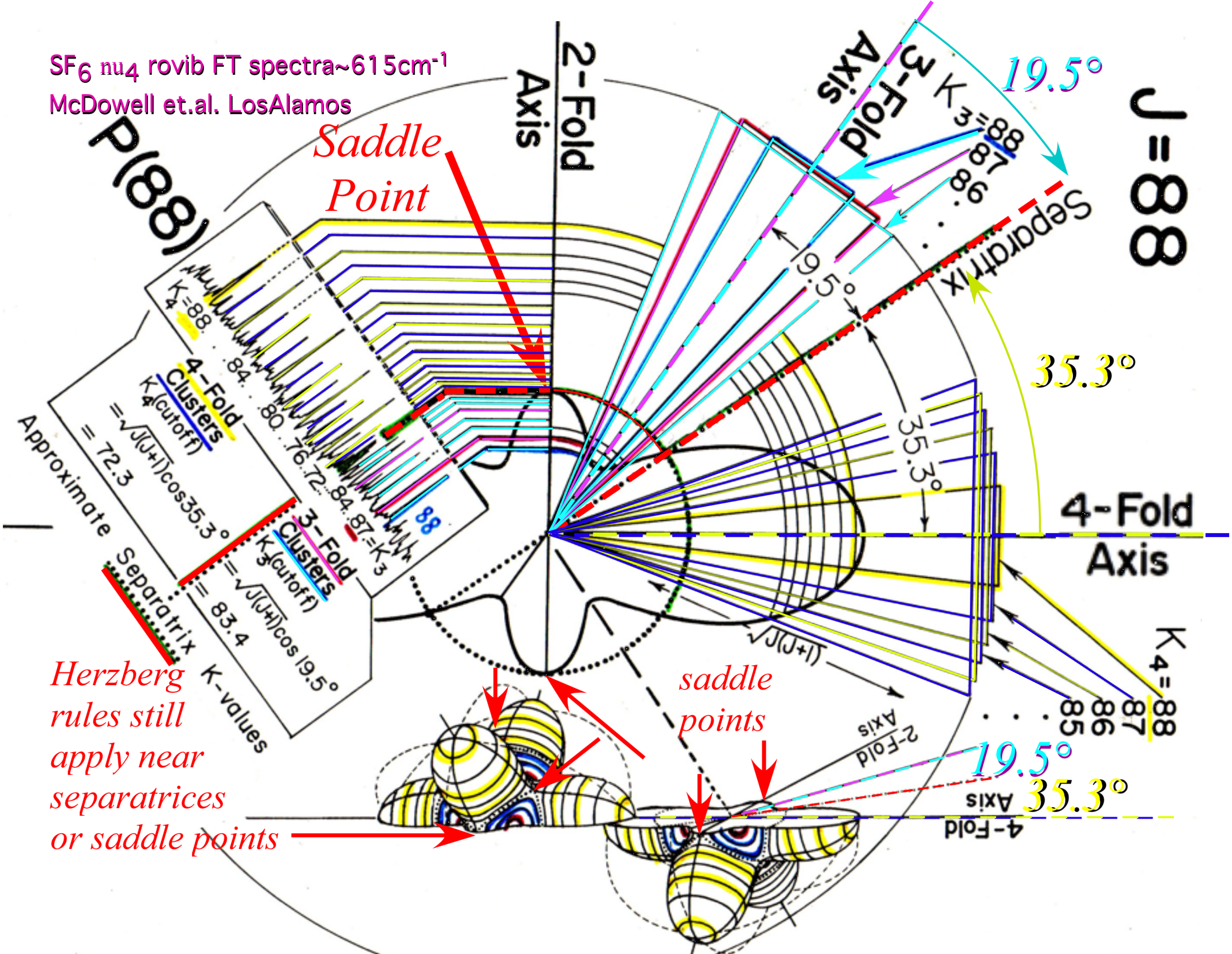
$$= B\mathbf{J}^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



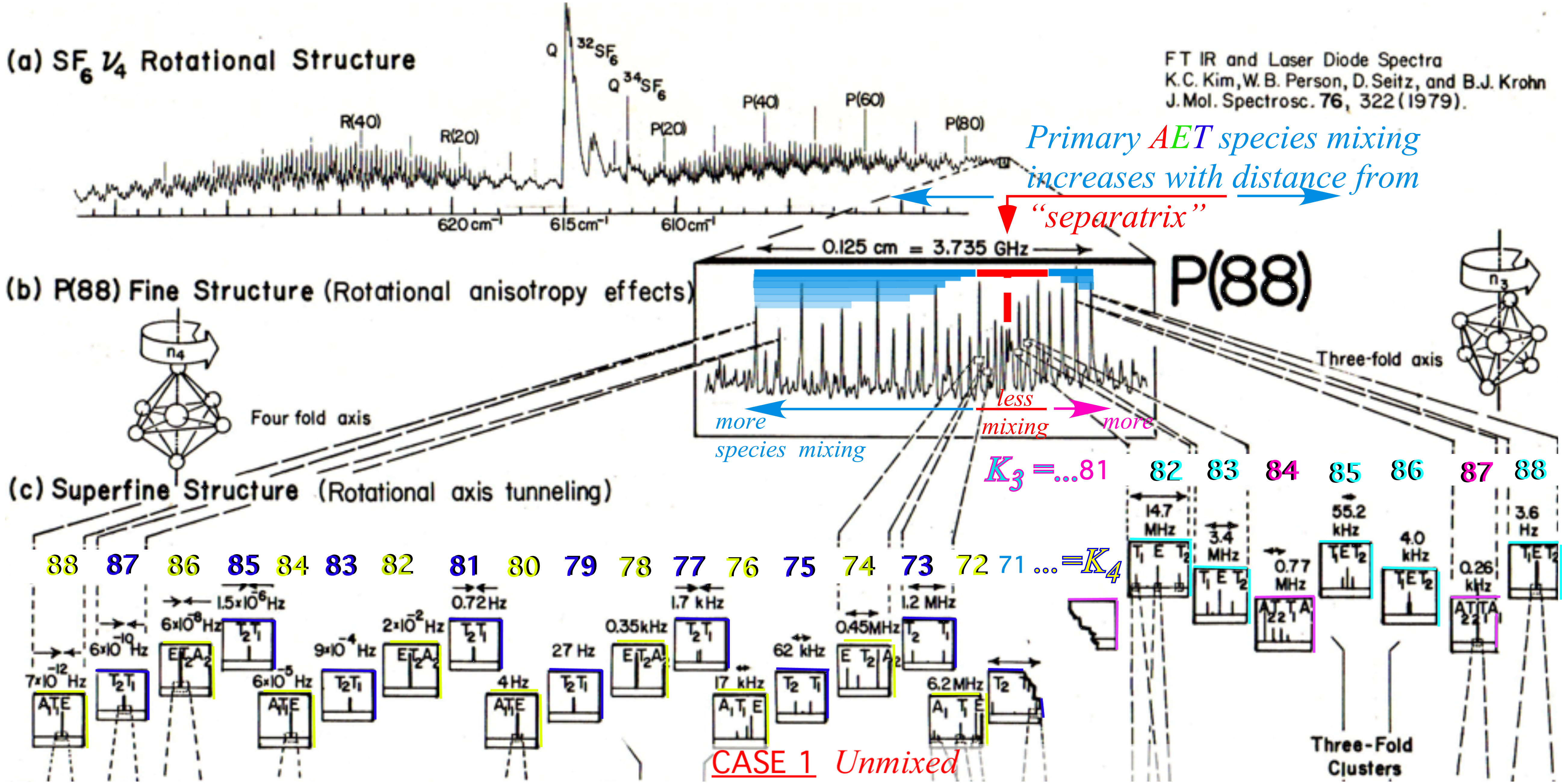
Rovibronic Energy (RE) Tensor Surface







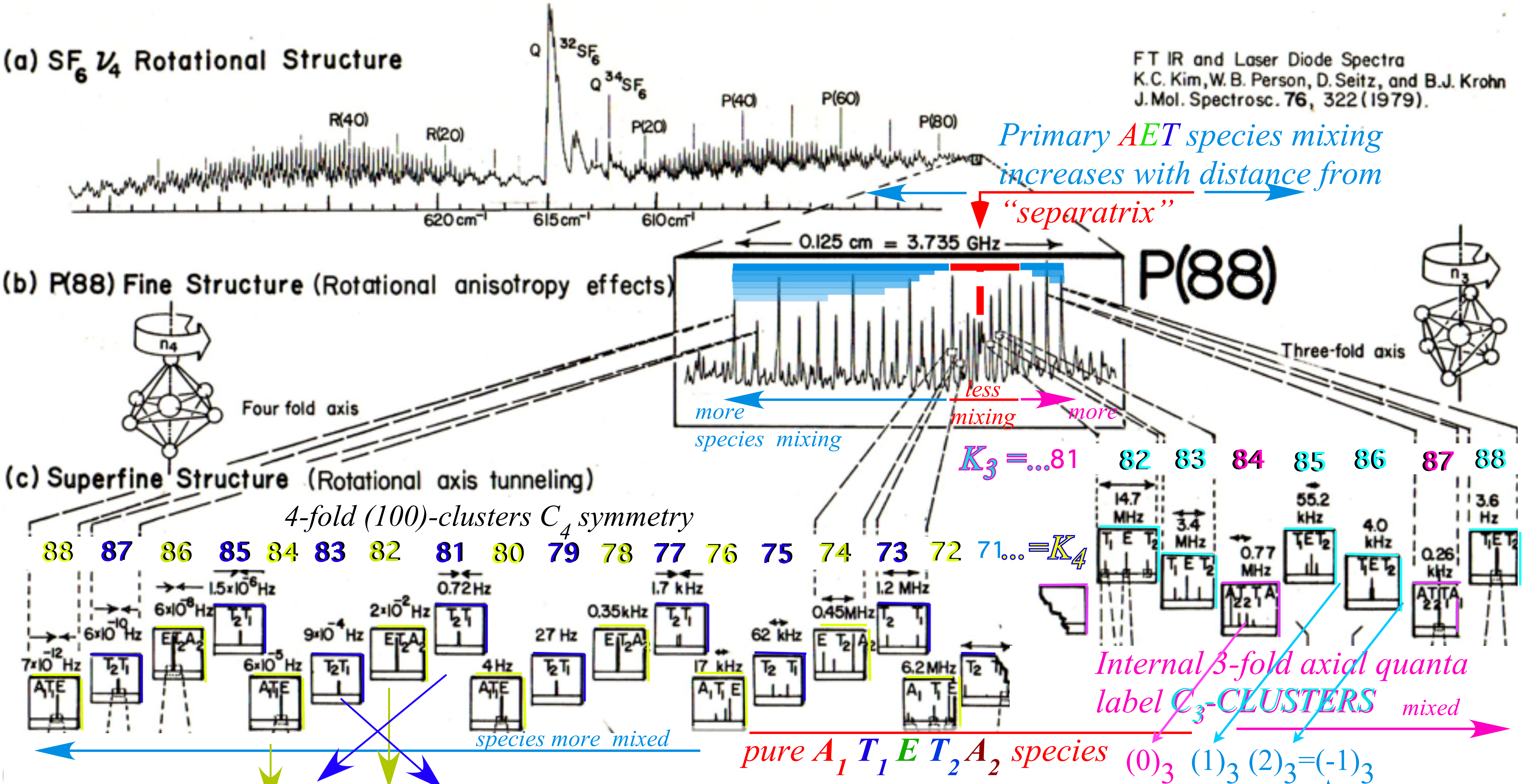
SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
J=88
2-Fold Axis
3-Fold Axis
4-Fold Axis
Saddle Point
Separatrix
19.5°
35.3°
K3=88
87
86
K4=88
85
86
87
88
4-Fold Clusters
K4(cutoff) = √J(J+1) cos35.3° = 72.3
3-Fold Clusters
K3(cutoff) = √J(J+1) cos 19.5° = 83.4
Approximate Separatrix K-values
√J(J+1)
Herzberg rules still apply near separatrices or saddle points
saddle points
2-Fold Axis
4-Fold Axis



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

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

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

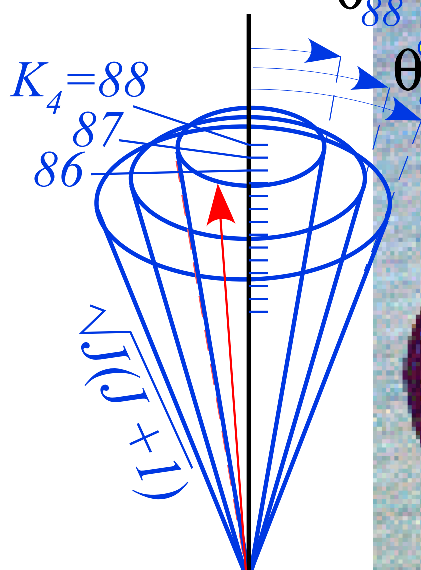
Spin-rotor S_N-tableau super-hyperfine theory: see p. 11 of Lecture 29

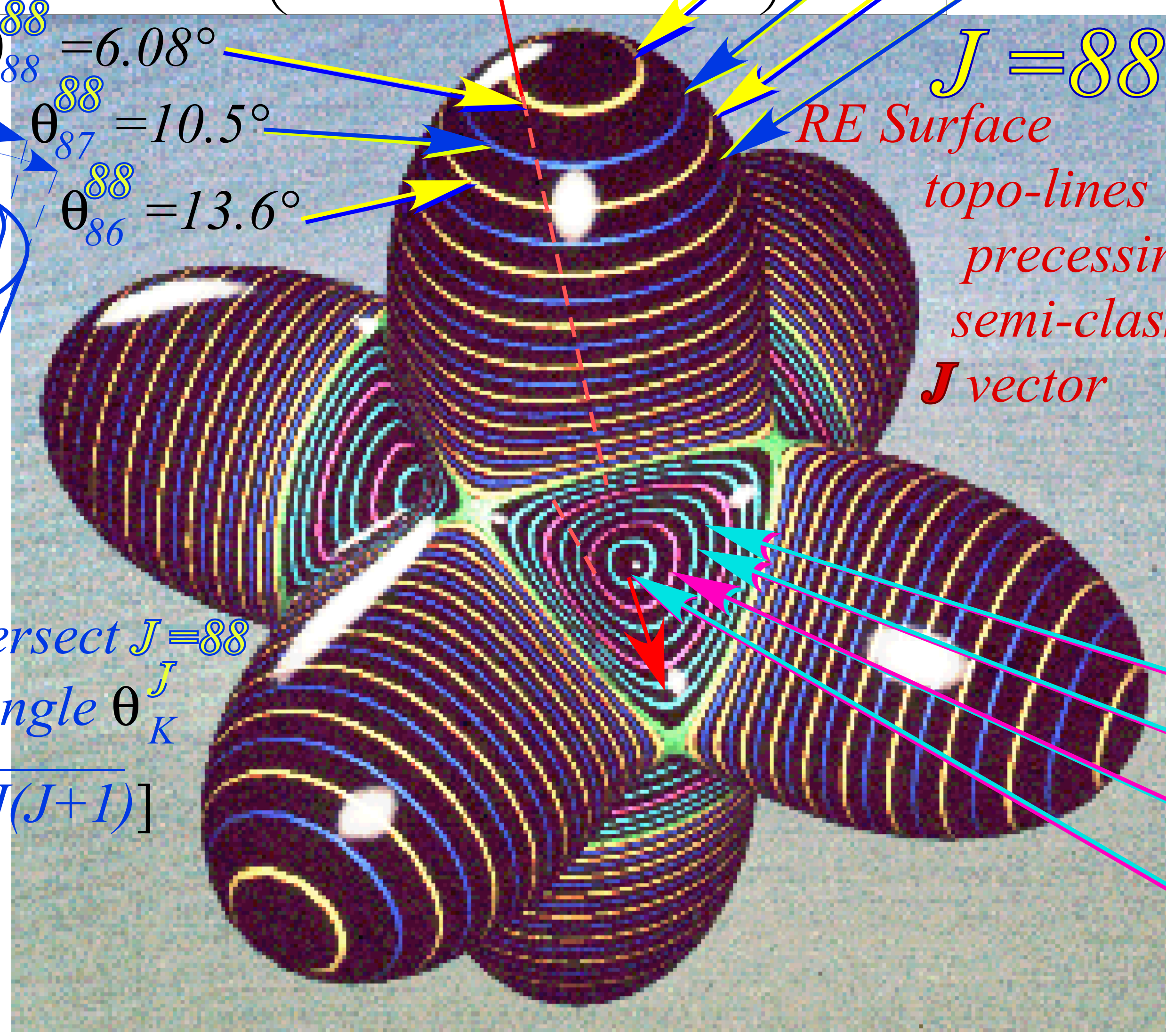
$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

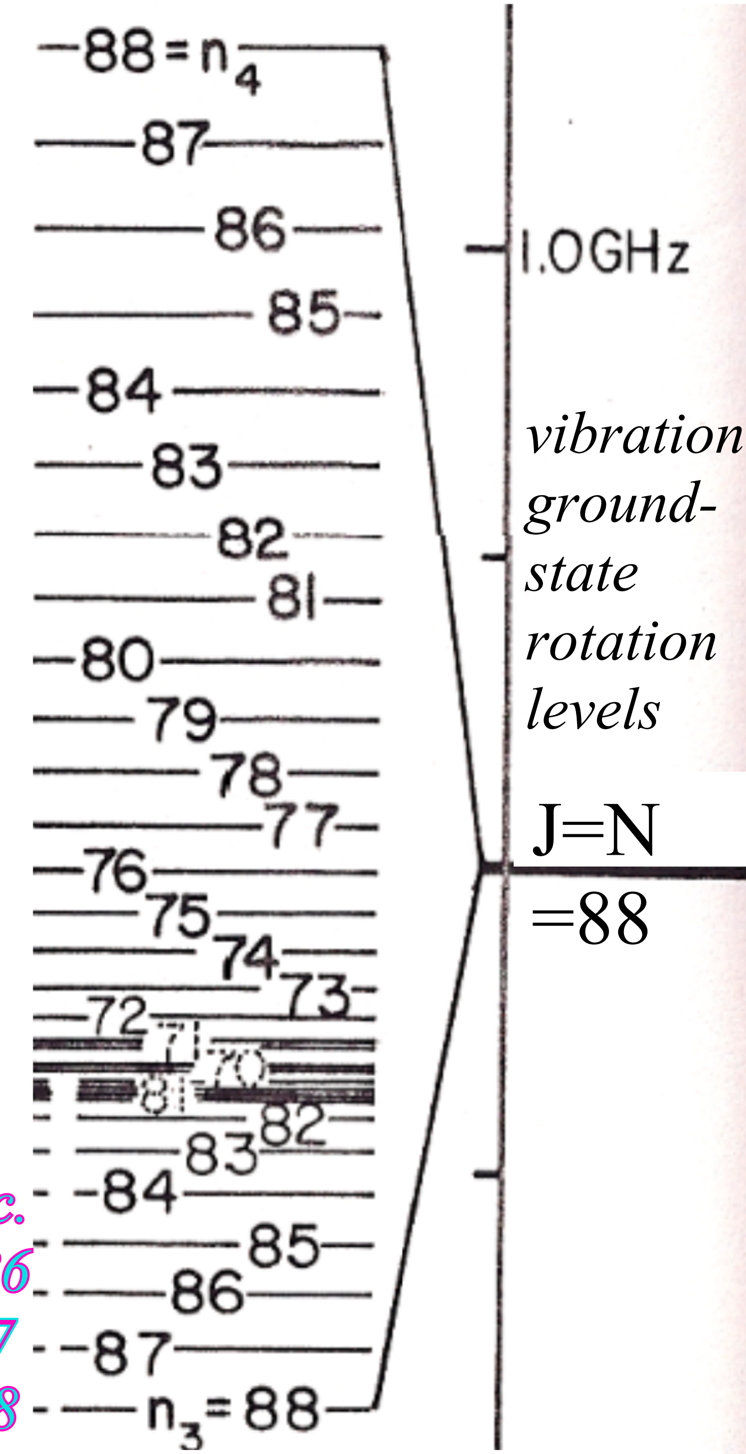
O_h or T_d Spherical Top: *(Hecht CH_4 Hamiltonian 1960)*

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

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







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

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

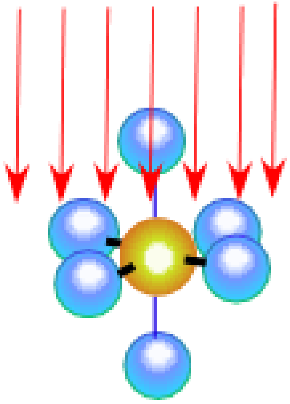
Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, STATE versus PARTICLE,

boils down to :

OUTSIDE versus INSIDE

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

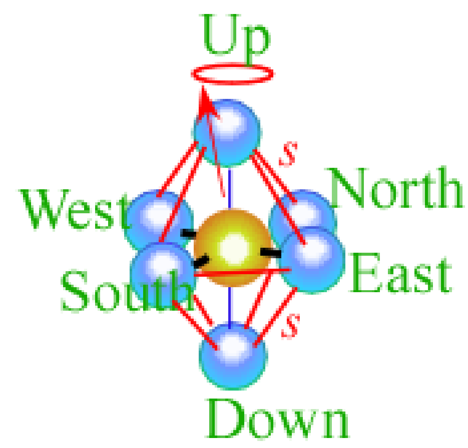


Example:
Cubic-Octahedral O reduced to Tetragonal C_4

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

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

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



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

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

Duality: The "Flip Side" of Symmetry Analysis.

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

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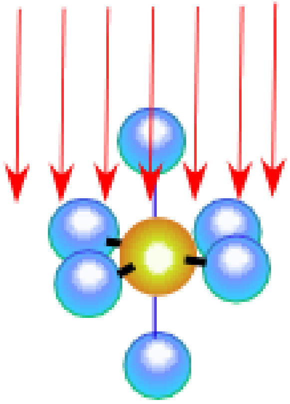
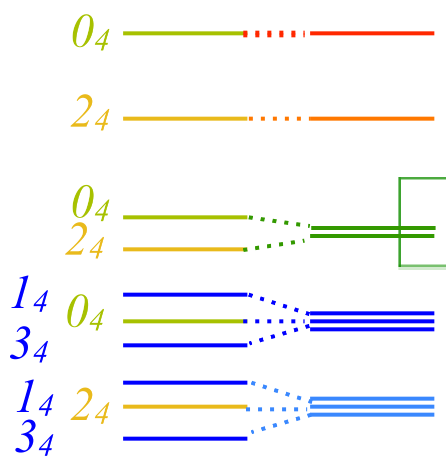
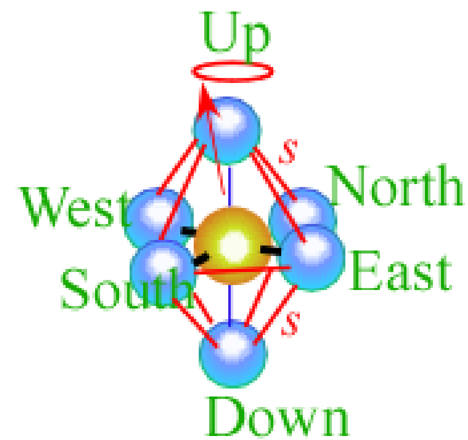




C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

*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

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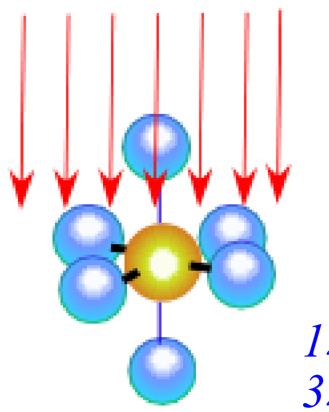
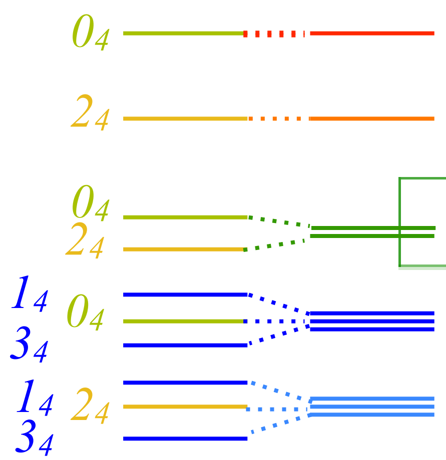
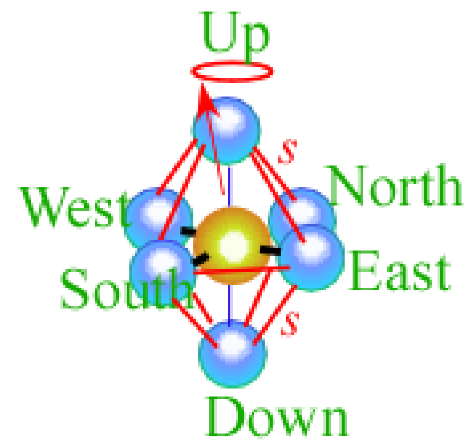




C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

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

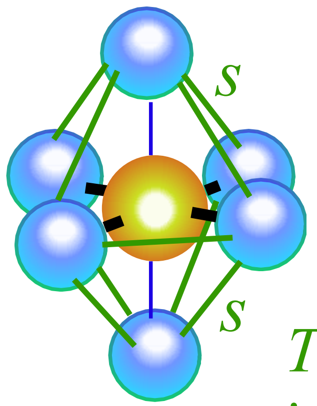


|U>	|D>	|E>	|W>	|N>	|S>
H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H

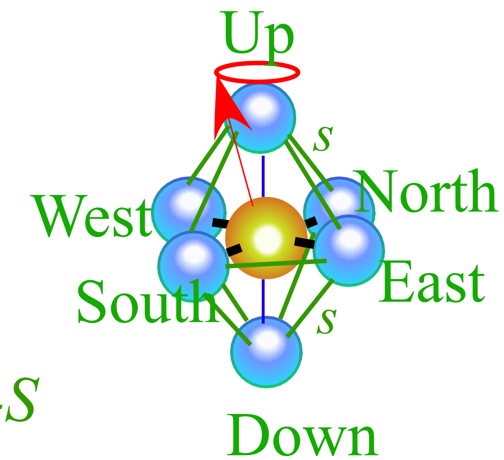
Tunneling (s) between axes
splits the 0_4 cluster

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

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



Tunneling s=-S is negative here



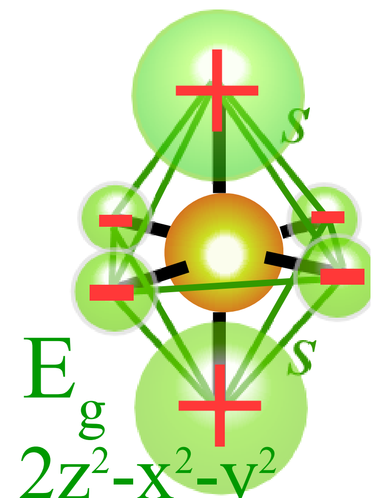
|U>|D>|E>|W>|N>|S>

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

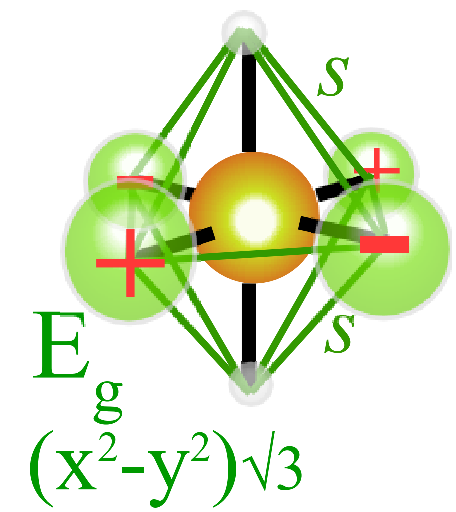
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}} = (H-2s) \begin{vmatrix} +2 \\ +2 \\ -1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

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

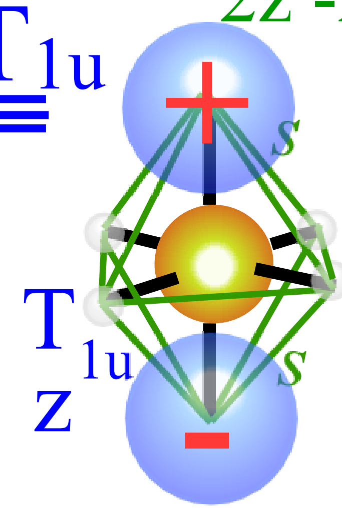
$$\begin{vmatrix} H & 0 & s & s & s & s \\ 0 & H & s & s & s & s \\ s & s & H & 0 & s & s \\ s & s & 0 & H & s & s \\ s & s & s & s & H & 0 \\ s & s & s & s & 0 & H \end{vmatrix} \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1 \\ 1 \end{vmatrix} \frac{1}{\sqrt{6}} = (H+4s) \begin{vmatrix} 1 \\ 1 \\ 1 \\ 1 \\ 1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



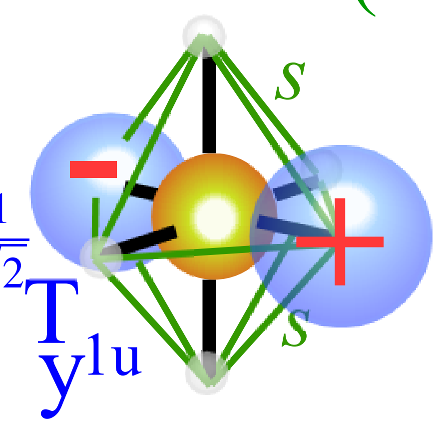
$\begin{vmatrix} +2 \\ +2 \\ -1 \\ -1 \\ -1 \\ -1 \end{vmatrix} \frac{1}{\sqrt{12}}$

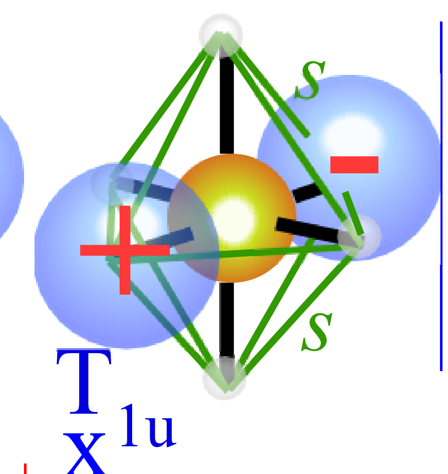


$\begin{vmatrix} 0 \\ 0 \\ -1 \\ -1 \\ +1 \\ +1 \end{vmatrix} \frac{1}{2}$

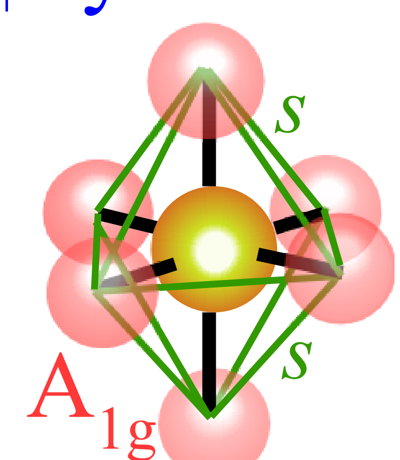


$\begin{vmatrix} 0 \\ 0 \\ +1 \\ -1 \\ 0 \\ 0 \end{vmatrix} \frac{1}{\sqrt{2}}$

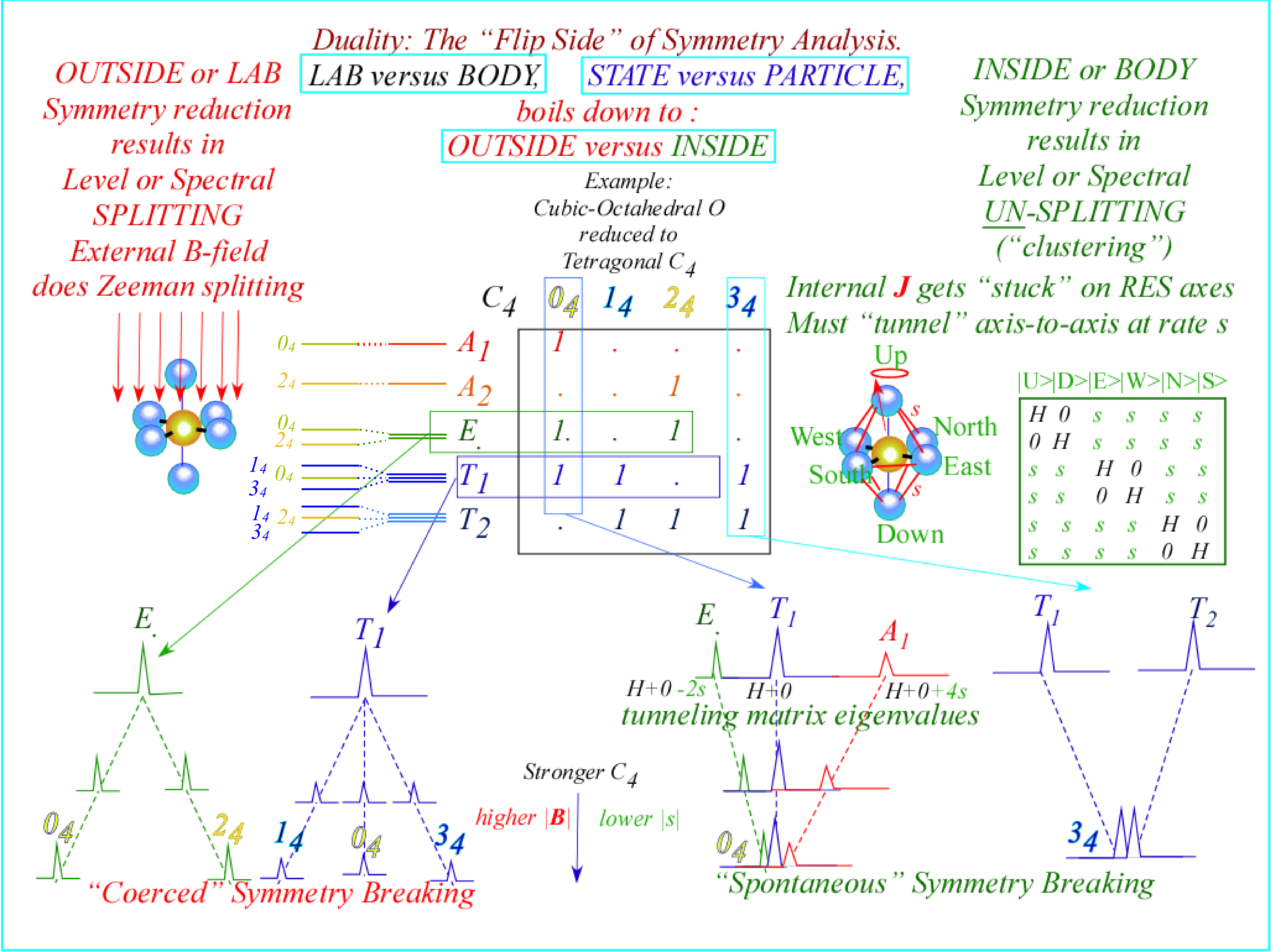




$\begin{vmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -1 \\ +1 \end{vmatrix} \frac{1}{\sqrt{2}}$



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



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Cubic-Octahedral O
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Tetragonal C_4
Internal J gets "stuck" on RES axes
Must "tunnel" axis-to-axis at rate s
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
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
H+0 -2s
H+0
H+0+4s
tunneling matrix eigenvalues
Stronger C_4
higher |B|
lower |s|
"Coerced" Symmetry Breaking
"Spontaneous" Symmetry Breaking

Details of P(88) ν_4 SF_6 and P(54) 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*

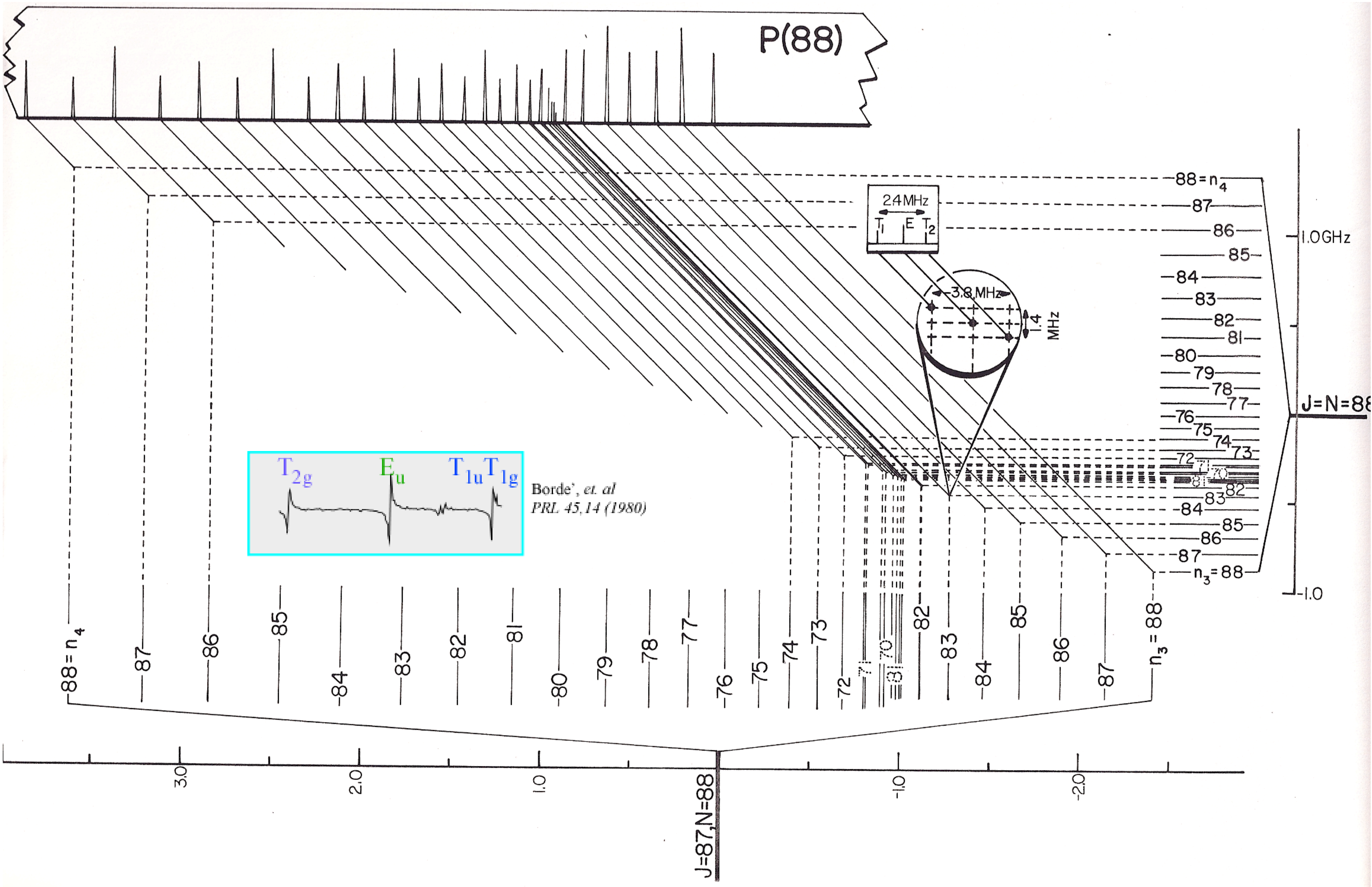
Hyperfine vs. superfine structure (Case 1. vs Case 2.)

Spin-0 nuclei give Bose Exclusion

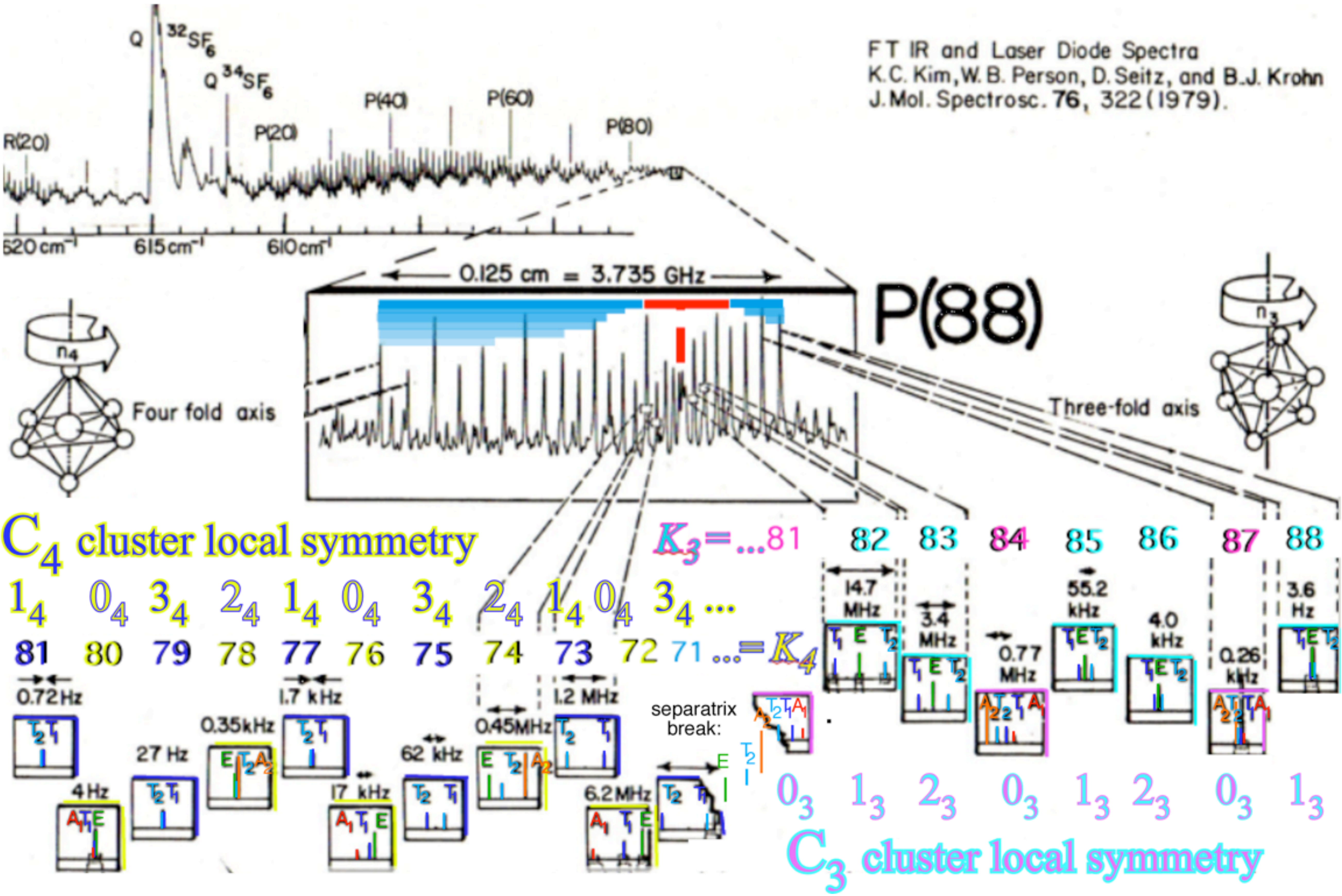
The spin-symmetry species mixing problem

Analogy between PE surface dynamics and RES

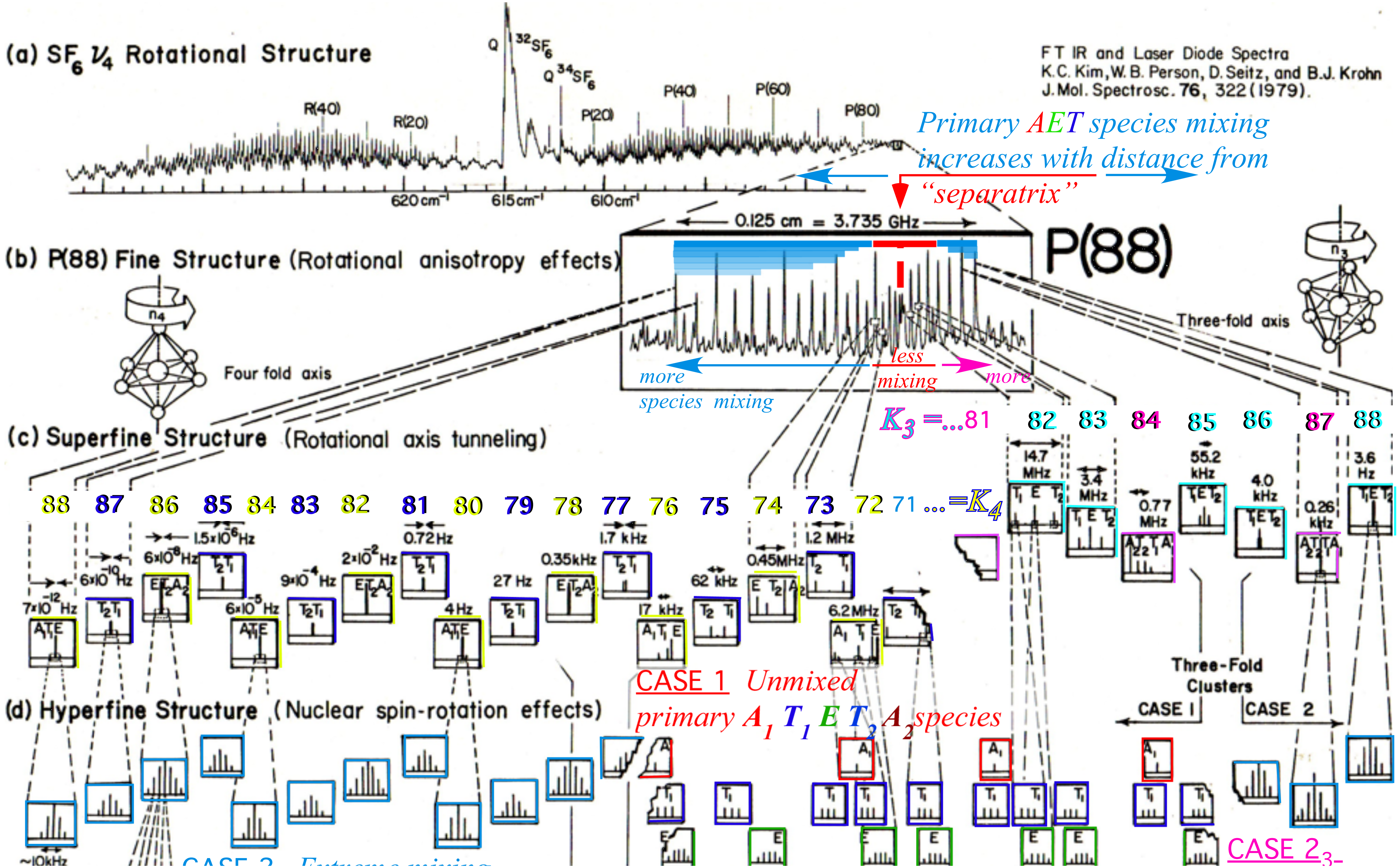
Rotational Energy Eigenvalue Surfaces (REES)

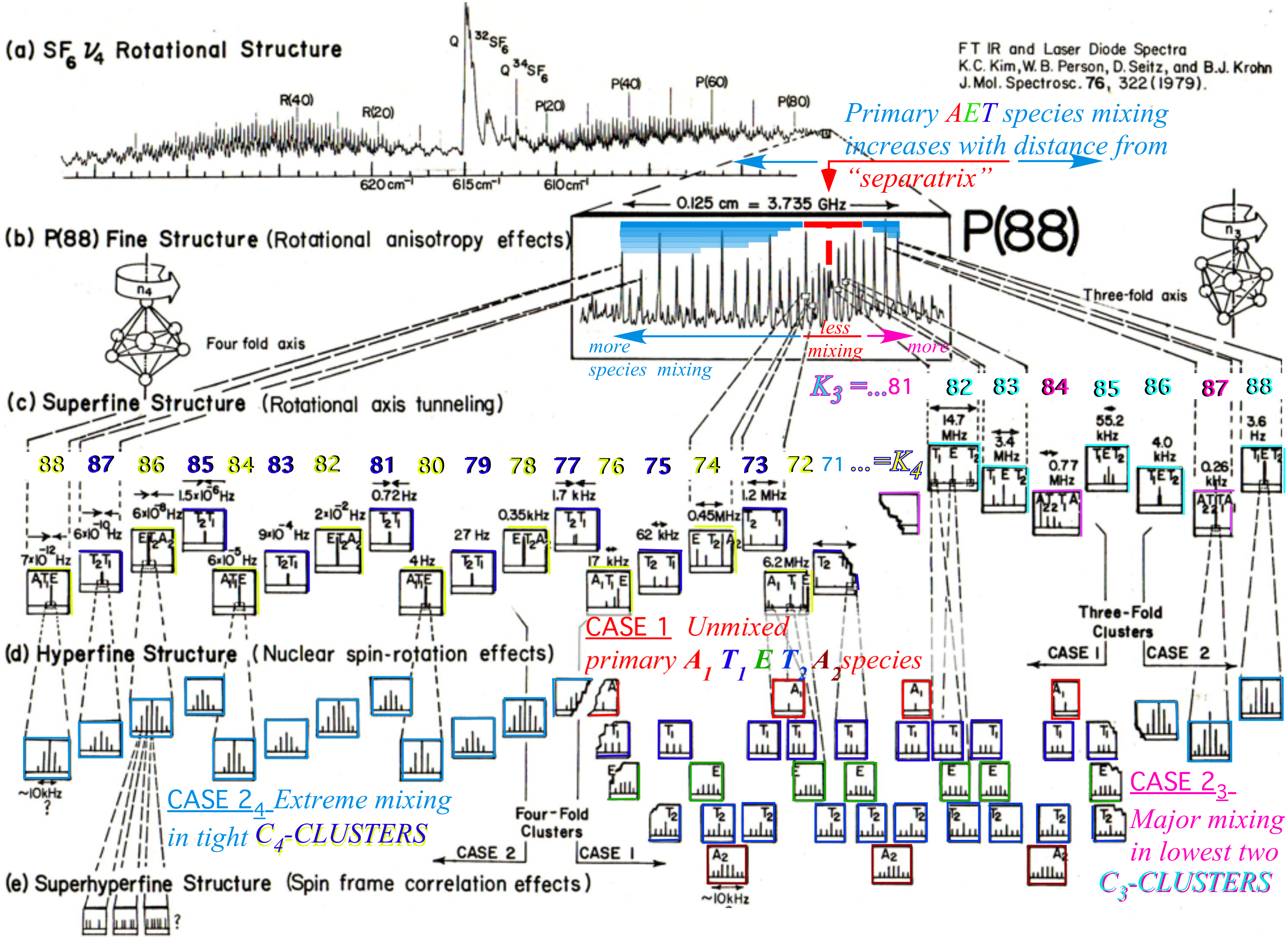

P(88)
88=n4
87
86
85
84
83
82
81
80
79
78
77
76
75
74
73
72
71
70
81
82
83
84
85
86
87
n3=88
2.4MHz
T1 E T2
3.8MHz
1.4 MHz
1.0GHz
J=N=88
-1.0
T2g Eu T1u T1g
Borde', et. al
PRL 45,14 (1980)
3.0
2.0
1.0
-1.0
-2.0
J=87,N=88

IR Spectra of SF6 ν_4 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).
Q 32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
Primary AET species mixing increases with distance from "separatrix"
0.125 cm = 3.735 GHz
(b) P(88) Fine Structure (Rotational anisotropy effects)
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
7×10-12 Hz
6×10-10 Hz
6×10-8 Hz
1.5×10-6 Hz
6×10-5 Hz
9×10-4 Hz
2×10-2 Hz
0.72 Hz
4 Hz
27 Hz
0.35 kHz
1.7 kHz
17 kHz
62 kHz
0.45 MHz
1.2 MHz
6.2 MHz
14.7 MHz
3.4 MHz
0.77 MHz
55.2 kHz
4.0 kHz
0.26 kHz
3.6 Hz
Three-Fold Clusters
CASE 1
CASE 2
CASE 1 Unmixed primary A1 T1 E T2 A2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
~10 kHz
CASE 23-



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Primary AET species mixing increases with distance from "separatrix"
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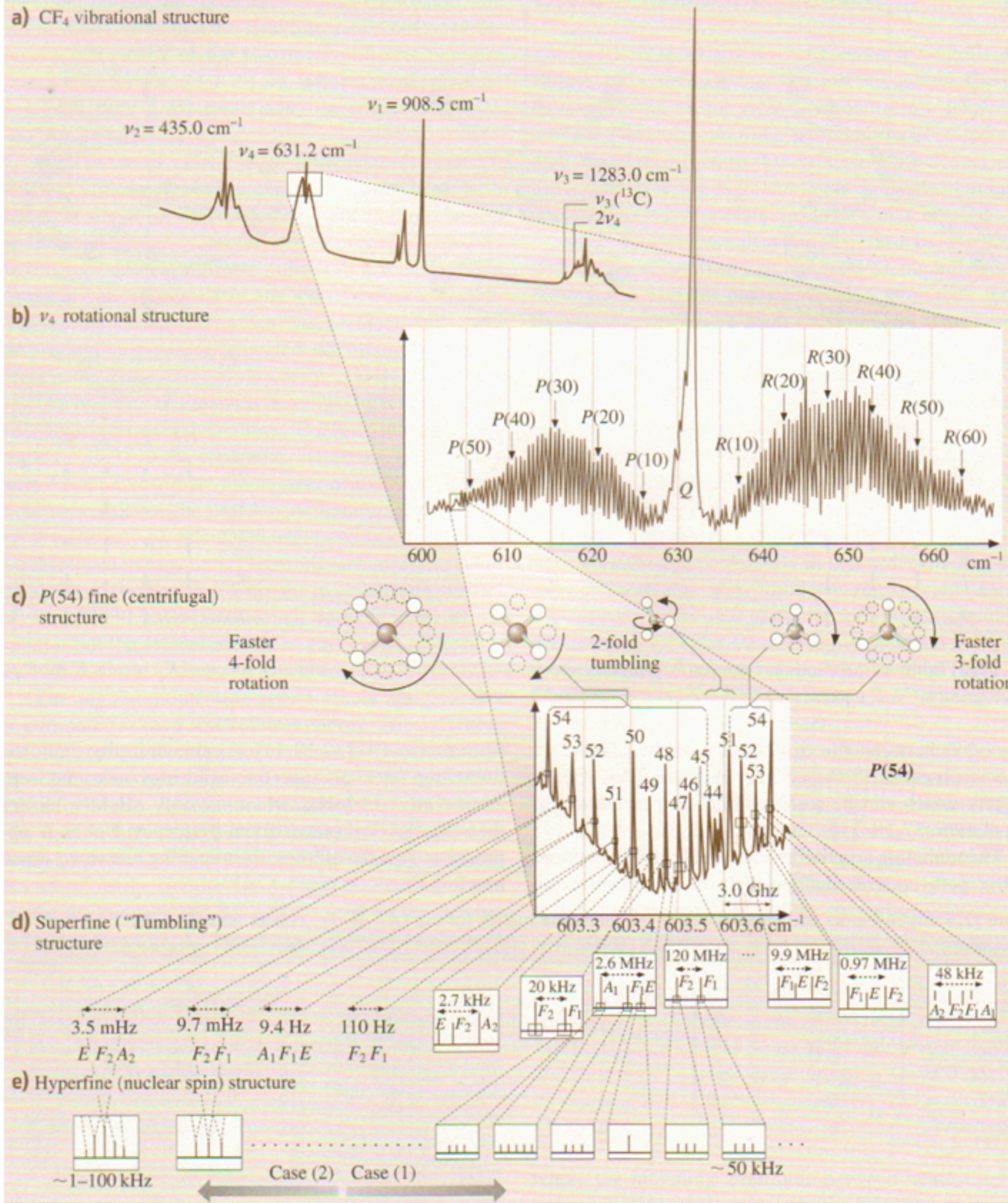
(b) P(88) Fine Structure (Rotational anisotropy effects)
Four fold axis
Three-fold axis
more species mixing
less mixing
more
(c) Superfine Structure (Rotational axis tunneling)
K3 =...81 82 83 84 85 86 87 88
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K4
CASE 1 Unmixed primary A1 T1 E T2 A2 species
Three-Fold Clusters
CASE I
CASE 2
(d) Hyperfine Structure (Nuclear spin-rotation effects)
CASE 24 Extreme mixing in tight C4-CLUSTERS
Four-Fold Clusters
CASE 2
CASE I
CASE 23 Major mixing in lowest two C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)

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)

P(54)



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Graphical approach to rotation-vibration-spin Hamiltonian

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

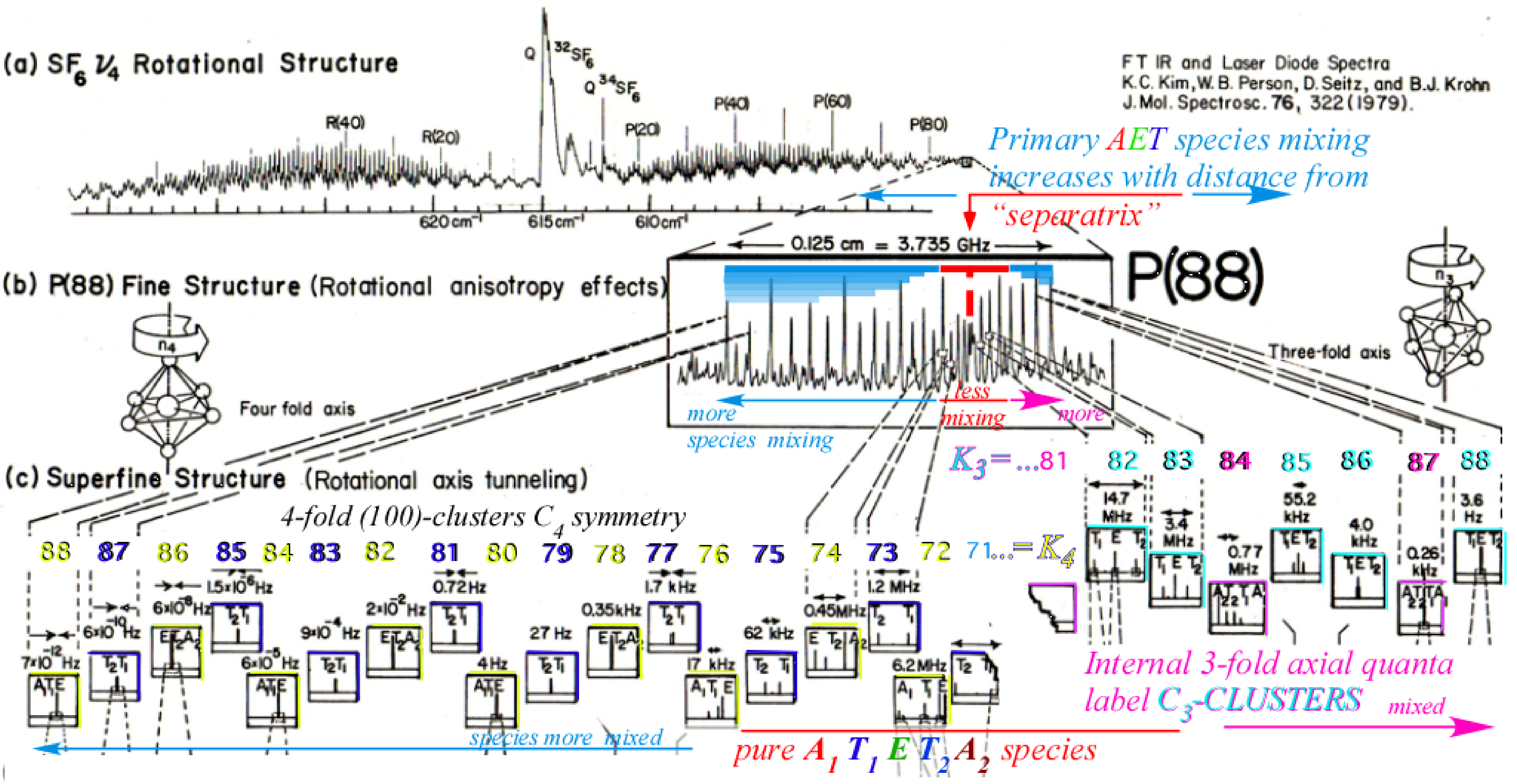
OUTLINE

Introductory review — Example(s)

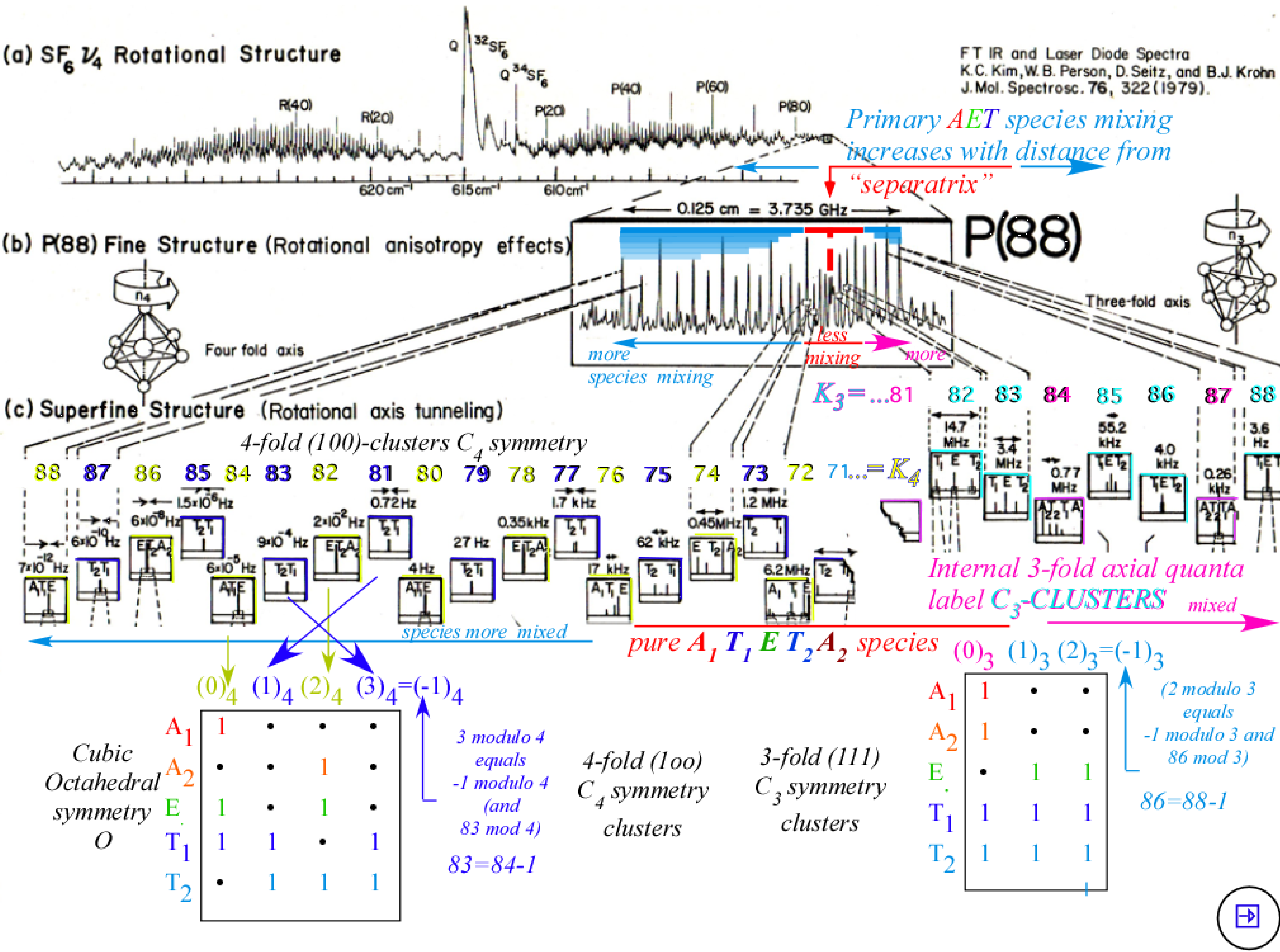
- *Rovibronic nomograms and PQR structure* — ν_3 and ν_4 SF_6
- *Rotational Energy Surfaces (RES) and θ^J_K-cones* — ν_4 P(88) SF_6
- *Spin symmetry correlation tunneling and entanglement* — SF_6

Recent developments

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



(a) SF6 ν4 Rotational Structure
Q 32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
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"
0.125 cm = 3.735 GHz
P(88)
(b) P(88) Fine Structure (Rotational anisotropy effects)
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
14.7 MHz
3.4 MHz
0.77 MHz
55.2 kHz
4.0 kHz
0.26 kHz
3.6 Hz
7×10-12 Hz
6×10-10 Hz
6×10-8 Hz
1.5×10-6 Hz
6×10-5 Hz
9×10-4 Hz
2×10-2 Hz
0.72 Hz
4 Hz
27 Hz
0.35 kHz
1.7 kHz
17 kHz
62 kHz
0.45 MHz
1.2 MHz
6.2 MHz
Internal 3-fold axial quanta
label C3-CLUSTERS
mixed
species more mixed
pure A1 T1 E T2 A2 species



(a) SF_6 ν_4 Rotational Structure
Q $^{32}SF_6$
Q $^{34}SF_6$
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm^{-1}
615 cm^{-1}
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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)
4-fold (100)-clusters C_4 symmetry
88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71... = K_4
K_3 = ...81 82 83 84 85 86 87 88
14.7 MHz
3.4 MHz
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55.2 kHz
4.0 kHz
0.26 kHz
3.6 Hz
7×10^{-12} Hz
6×10^{-10} Hz
6×10^{-8} Hz
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4 Hz
27 Hz
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1.7 kHz
17 kHz
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1.2 MHz
6.2 MHz
Internal 3-fold axial quanta label C_3-CLUSTERS
mixed
species more mixed
pure A_1 T_1 E T_2 A_2 species
$(0)_4$ $(1)_4$ $(2)_4$ $(3)_4=(-1)_4$
Cubic Octahedral symmetry O
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

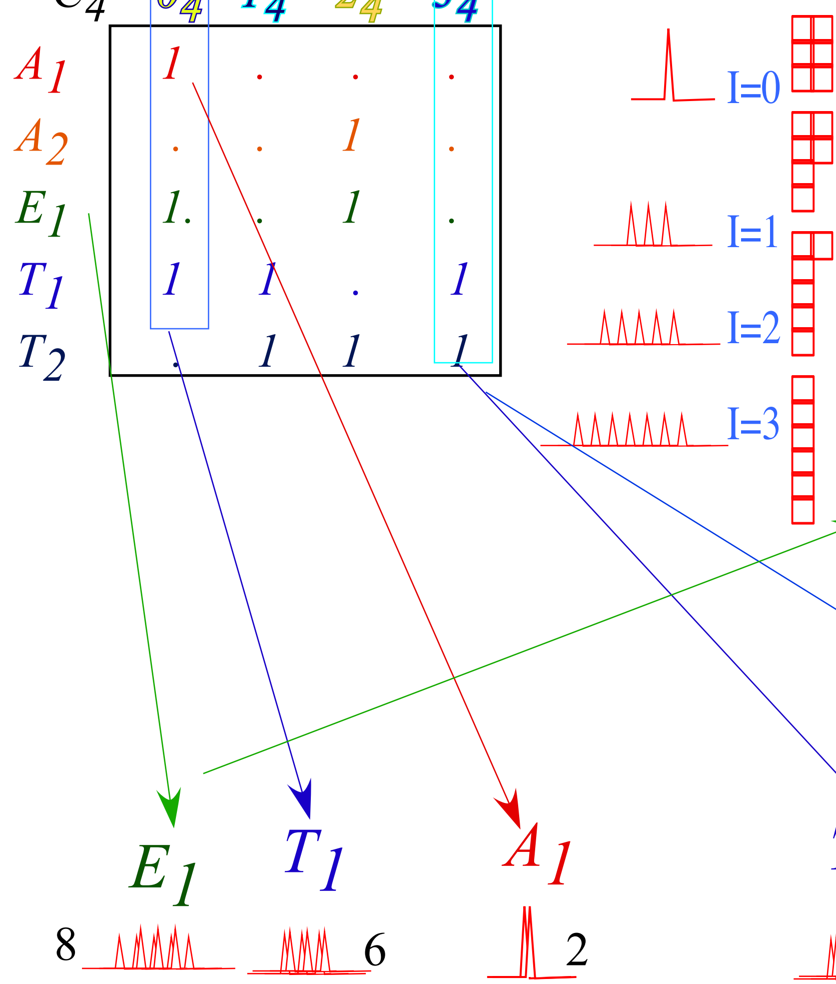
total-spin-I-symmetry O_h species

in SF_6.

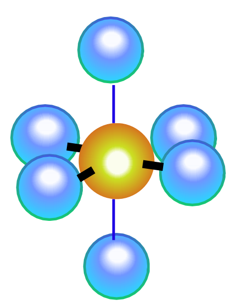
C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E_1	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

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

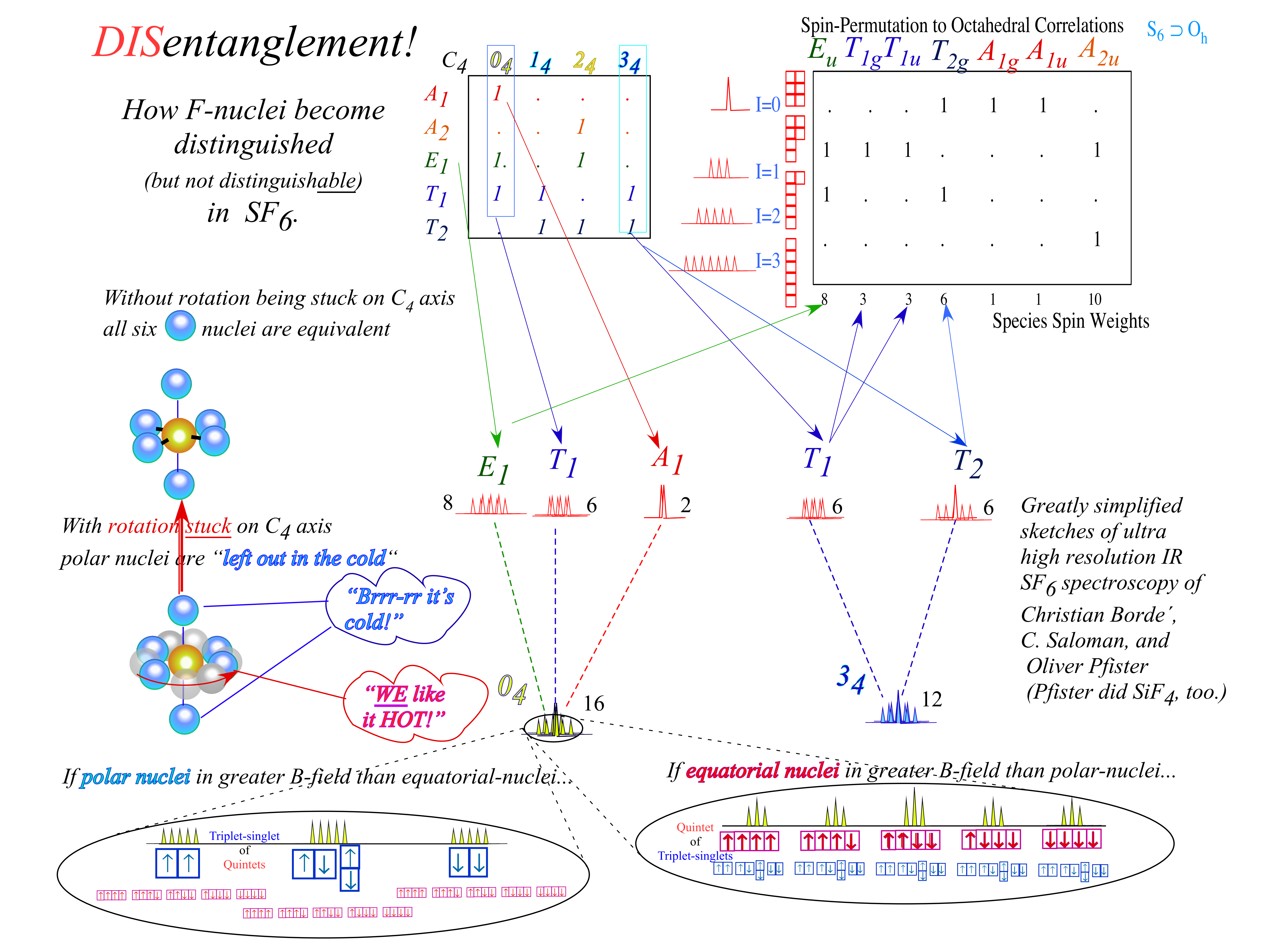


With rotation all six nuclei are equivalent

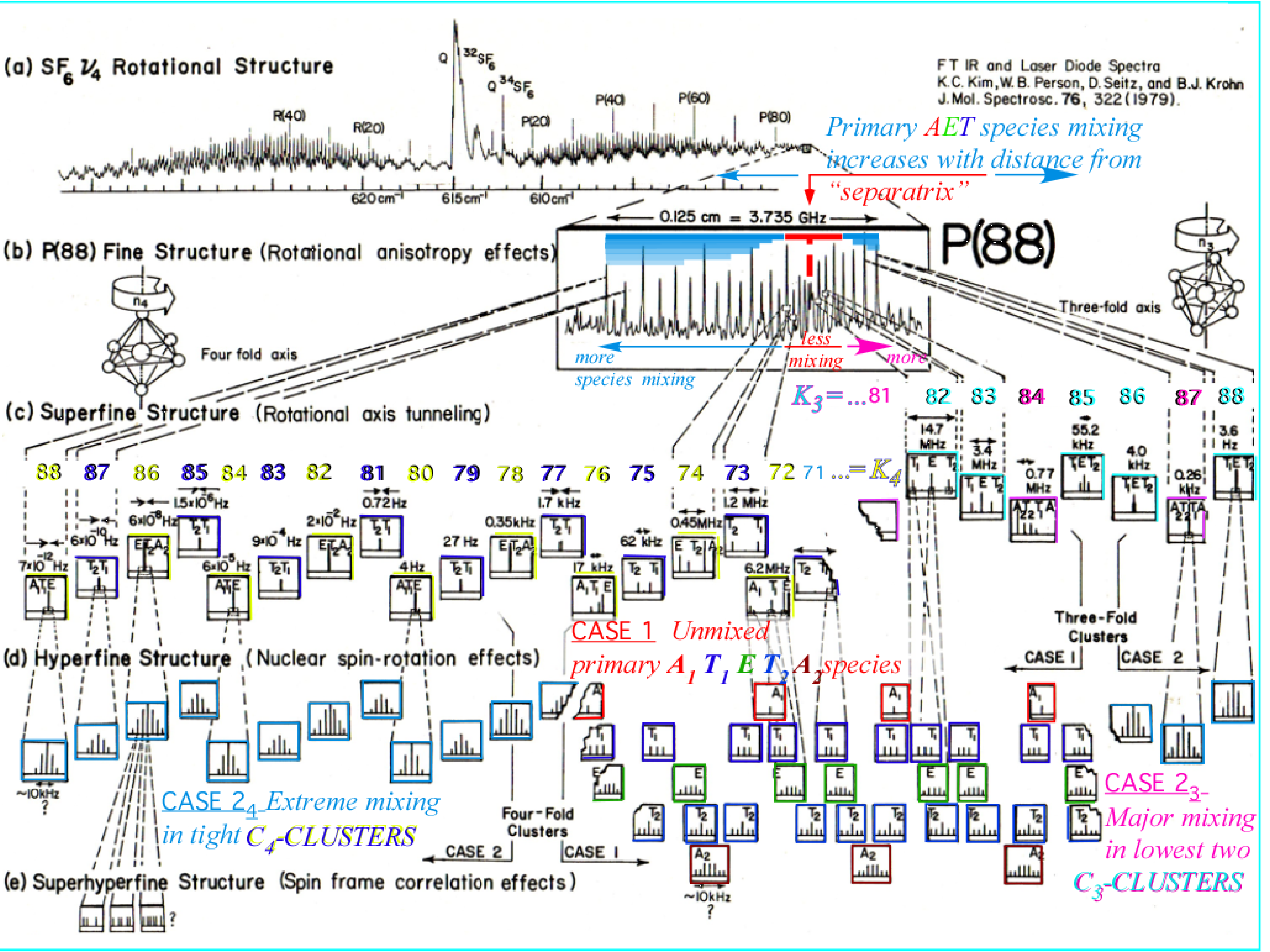


Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister (Pfister did SiF_4, too.)

Spin-rotor S_N-tableau super-hyperfine theory: see p. 11 of Lecture 29 (S_N-tableaus on p. 37)



DISentanglement!
How F-nuclei become distinguished
(but not distinguishable)
in SF6.
Spin-Permutation to Octahedral Correlations
S6 ⊃ Oh
C4 04 14 24 34
A1 1 . . .
A2 . . 1 .
E1 1. . 1 .
T1 1 1 . 1
T2 . 1 1 1
Eu T1g T1u T2g A1g A1u A2u
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
Without rotation being stuck on C4 axis
all six nuclei are equivalent
With rotation stuck on C4 axis
polar nuclei are "left out in the cold"
"Brrr-rr it's cold!"
"WE like it HOT!"
E1 T1 A1 T1 T2
8 6 2 6 6
04 16
34 12
Greatly simplified sketches of ultra high resolution IR SF6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister (Pfister did SiF4, too.)
If polar nuclei in greater B-field than equatorial-nuclei...
Triplet-singlet of Quintets
If equatorial nuclei in greater B-field than polar-nuclei...
Quintet of Triplet-singlets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Three-fold axis
more species mixing
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K3=...81 82 83 84 85 86 87 88
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3.4 MHz
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88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71 ...=K4
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1.5×10-6 Hz
6×10-5 Hz
9×10-4 Hz
2×10-2 Hz
0.72 Hz
4 Hz
27 Hz
0.35 kHz
1.7 kHz
17 kHz
62 kHz
0.45 MHz
1.2 MHz
6.2 MHz
CASE 1 Unmixed
primary A1 T1 E T2 A2 species
Three-Fold Clusters
CASE 1
CASE 2
(d) Hyperfine Structure (Nuclear spin-rotation effects)
~10kHz
?
CASE 24 Extreme mixing
in tight C4-CLUSTERS
Four-Fold Clusters
CASE 2
CASE 1
CASE 23-
Major mixing
in lowest two
C3-CLUSTERS
(e) Superhyperfine Structure (Spin frame correlation effects)
~10kHz
?

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

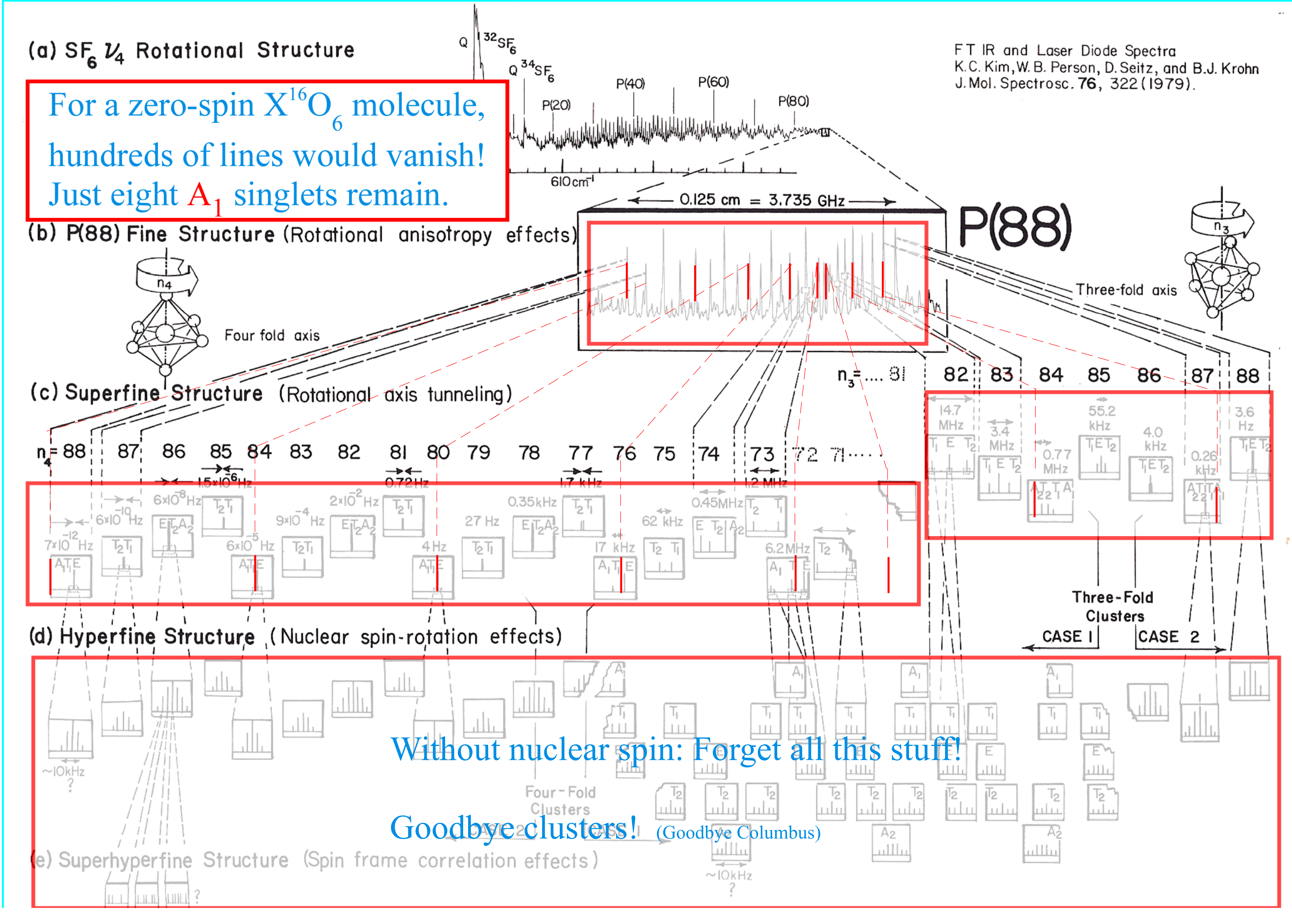
Hyperfine vs. superfine structure (Case 1. vs Case 2.)

➡ *Spin-0 nuclei give Bose Exclusion*

The spin-symmetry species mixing problem

Analogy between PE surface dynamics and RES

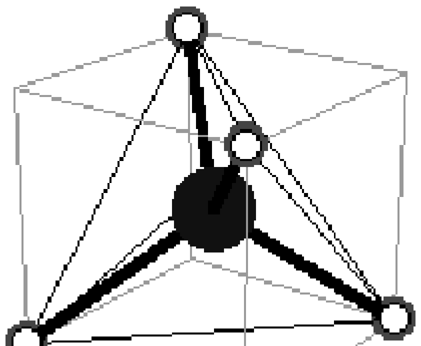
Rotational Energy Eigenvalue Surfaces (REES)



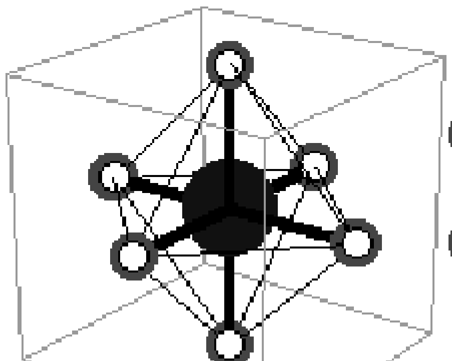
(a) SF6 ν4 Rotational Structure
FT IR and Laser Diode Spectra
K.C. Kim, W.B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
For a zero-spin X16O6 molecule, hundreds of lines would vanish!
Just eight A1 singlets remain.
Q 32SF6
Q 34SF6
P(20)
P(40)
P(60)
P(80)
610 cm-1
0.125 cm = 3.735 GHz
P(88)
(b) P(88) Fine Structure (Rotational anisotropy effects)
Four fold axis
Three-fold axis
(c) Superfine Structure (Rotational axis tunneling)
n3= 81 82 83 84 85 86 87 88
n4= 88 87 86 85 84 83 82 81 80 79 78 77 76 75 74 73 72 71....
Three-Fold Clusters
CASE 1
CASE 2
(d) Hyperfine Structure (Nuclear spin-rotation effects)
Four-Fold Clusters
Without nuclear spin: Forget all this stuff!
Goodbye clusters! (Goodbye Columbus)
(e) Superhyperfine Structure (Spin frame correlation effects)

Some examples of Bose Exclusion

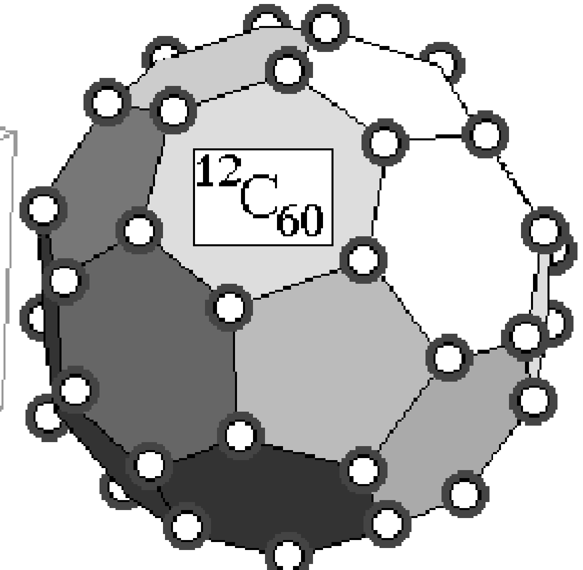
Spherical Top Molecules with Spin-0 Nuclei



OsO_4

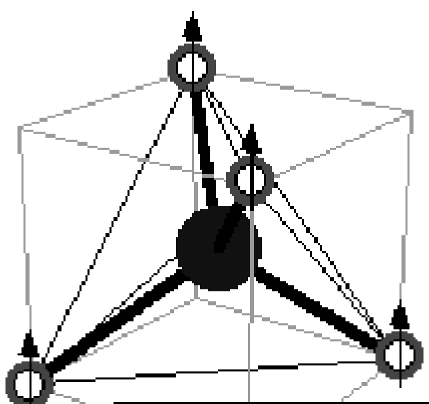


none?...



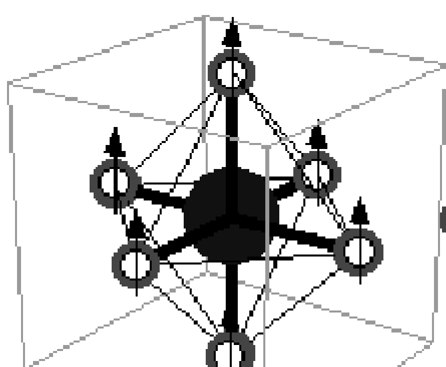
Only 1 hyperfine state: I=0

Spherical Top Molecules with Spin-1/2 Nuclei



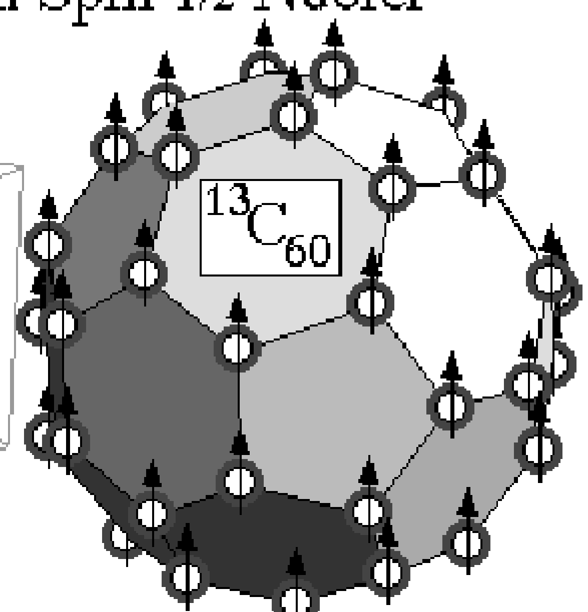
CF_4, SiF_4..

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



SF_6..

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



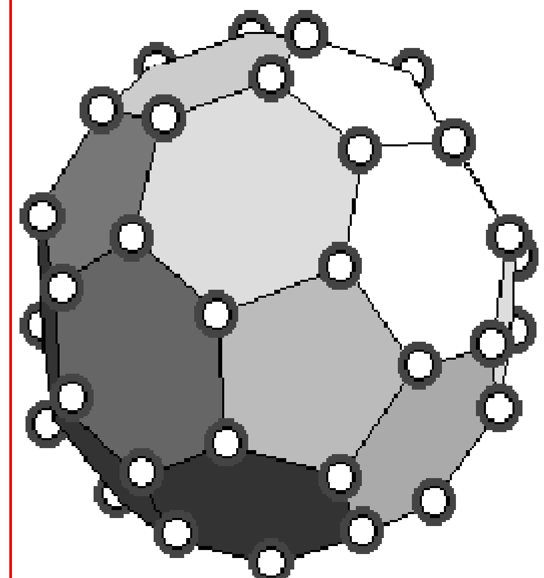
2^{60}=1.15x10^{18} hyperfine states: I=0-30

Some examples of Fermi (non) Exclusion

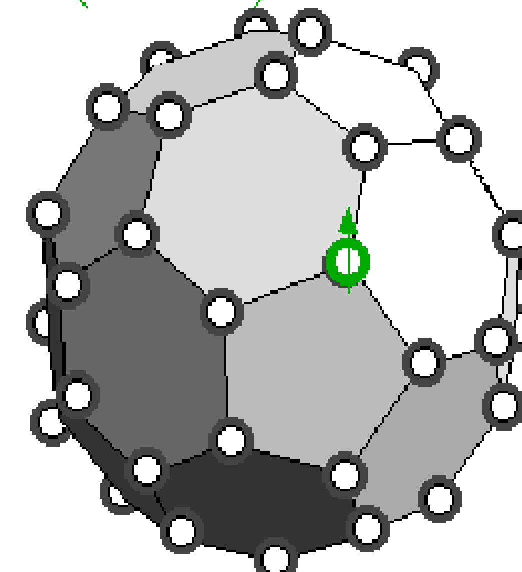
Example of extreme symmetry exclusion

... (and partial recovery)

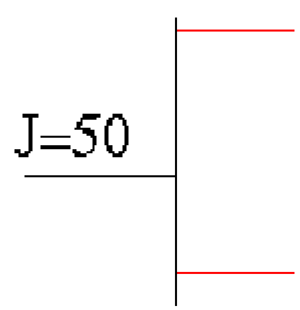
Y_h Symmetry reduced to C_v by a single neutron (in ^{13}C)



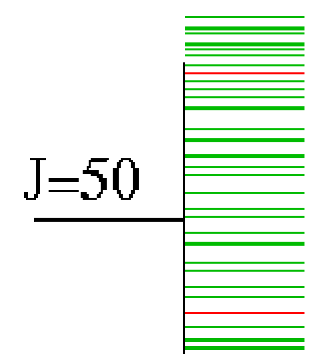
$^{12}C_{60}$



$^{13}C^{12}C_{59}$



2 levels allowed by Pauli Exclusion



202 levels allowed

Question: Where did those 200 levels go?

Better Question: Where did those 1.15 octillion levels go?

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

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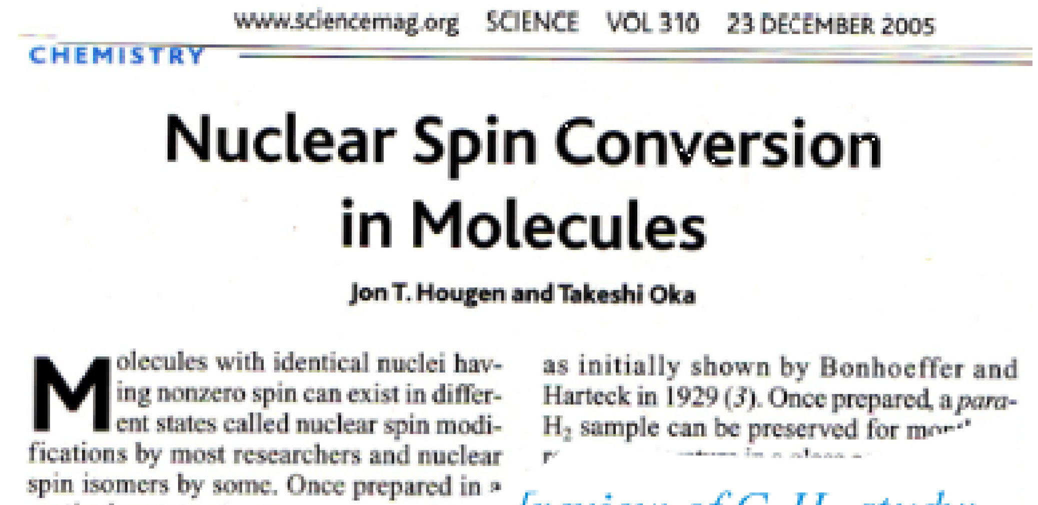
CONSERVATION OF ROVIBRONIC SPECIES - *Two Views:*

Old *(1939, 1945, and 1966)* *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)]*

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

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

Conservation and preservation?

...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

To conserve vs. To convert

To preserve vs. To pervert

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

Conversion, perversion or transition?

...during transitions involving...

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

Widespread and extreme mixing (perversion) 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?***

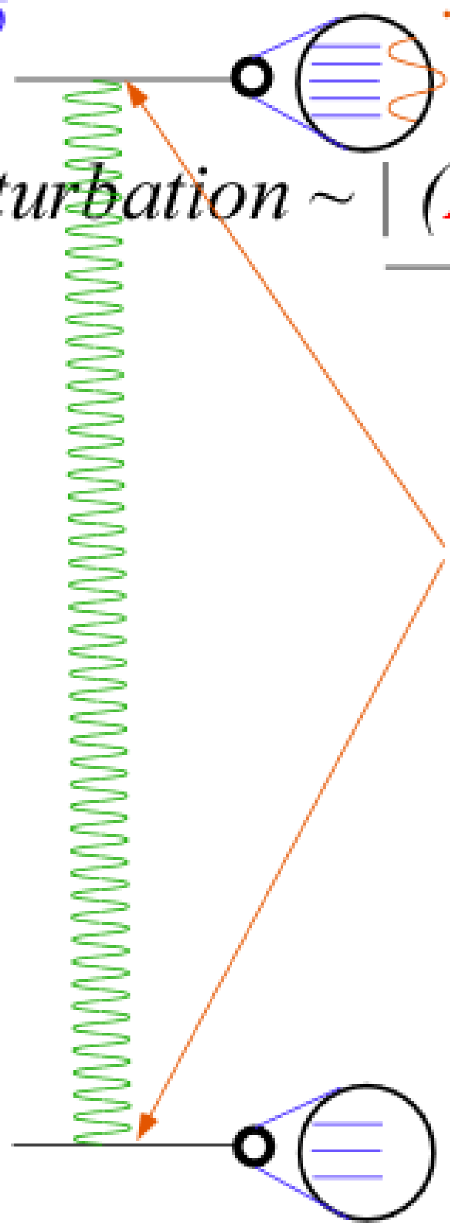
$A_{2u}{}^{1}$

No Way!

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

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

$E_{2g}{}^{5}$



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

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

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

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

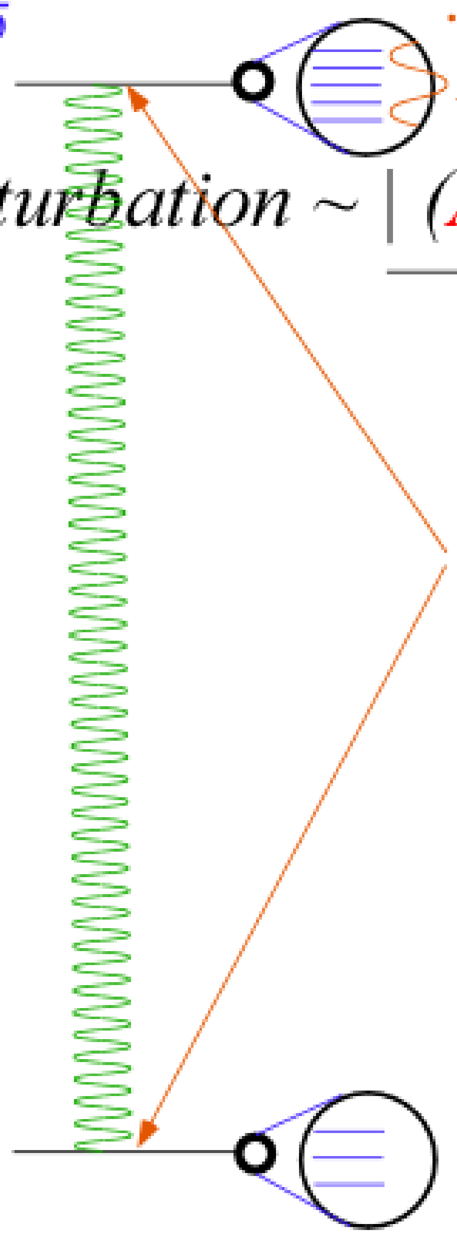
What preserves it? versus What mixes it up?

A_{2u}^{1}

No Way!

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

E_{2g}^{5}



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

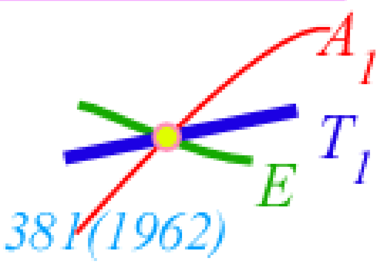
$$\text{perturbation} \sim \frac{|\,(A_{1g}^{3}|\text{spin-rovib.}|E_{2g}^{5})\,|^2}{E_{A_{1g}^{3}} - E_{E_{2g}^{5}}}$$

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

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)

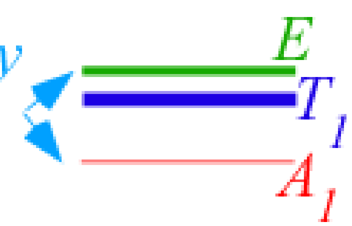
Level-clustering

Dorney and Watson JMS 42,135(1972)

Harter and Patterson PRL38,224(1977)

JCP 66,4872(1977)

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



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)

Graphical approach to rotation-vibration-spin Hamiltonian

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

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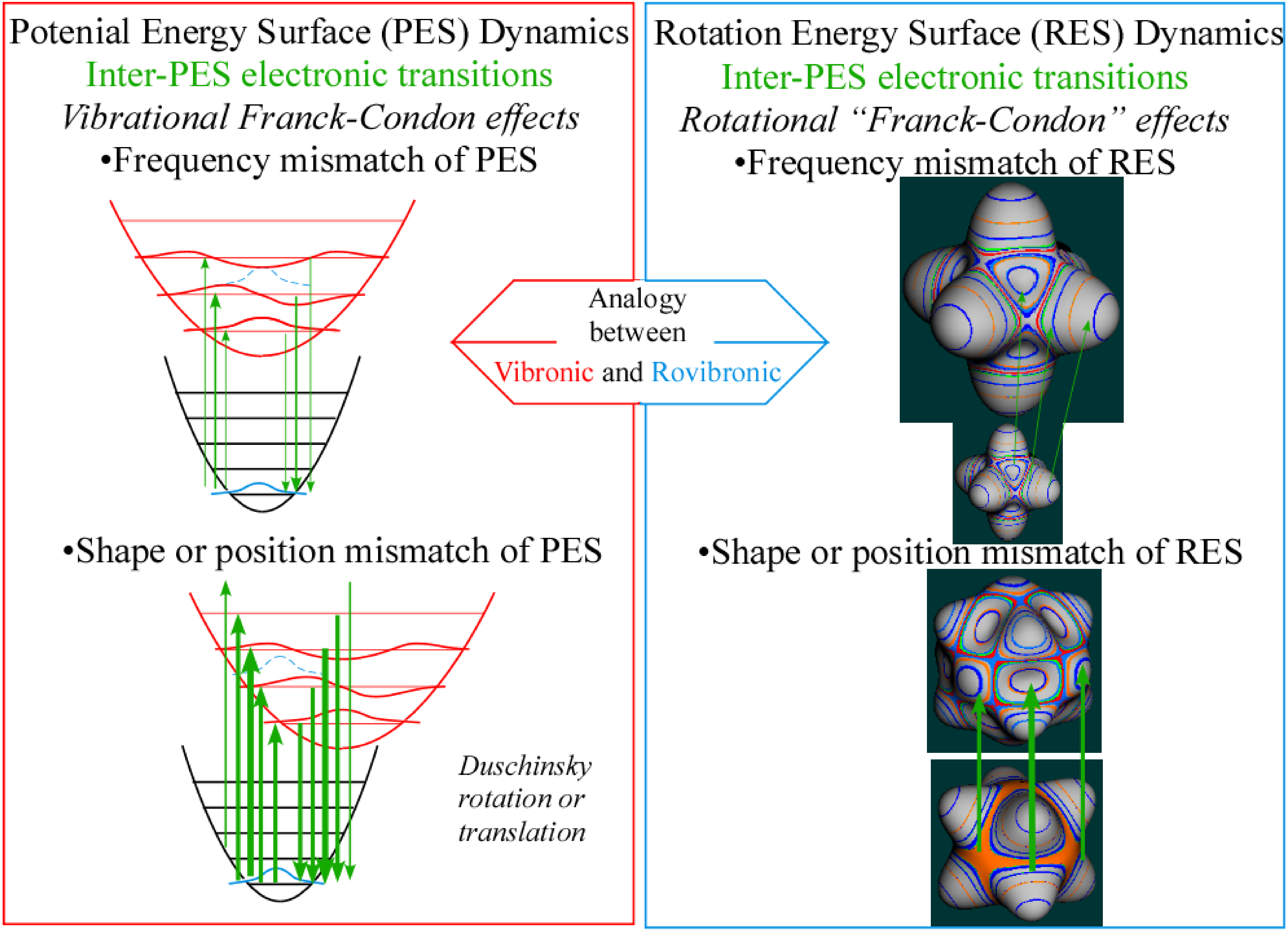
- *Rotational Energy Surfaces (RES) and θ^J_K-cones* — ν_4 P(88) SF_6
- *Spin symmetry correlation tunneling and entanglement* — SF_6

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

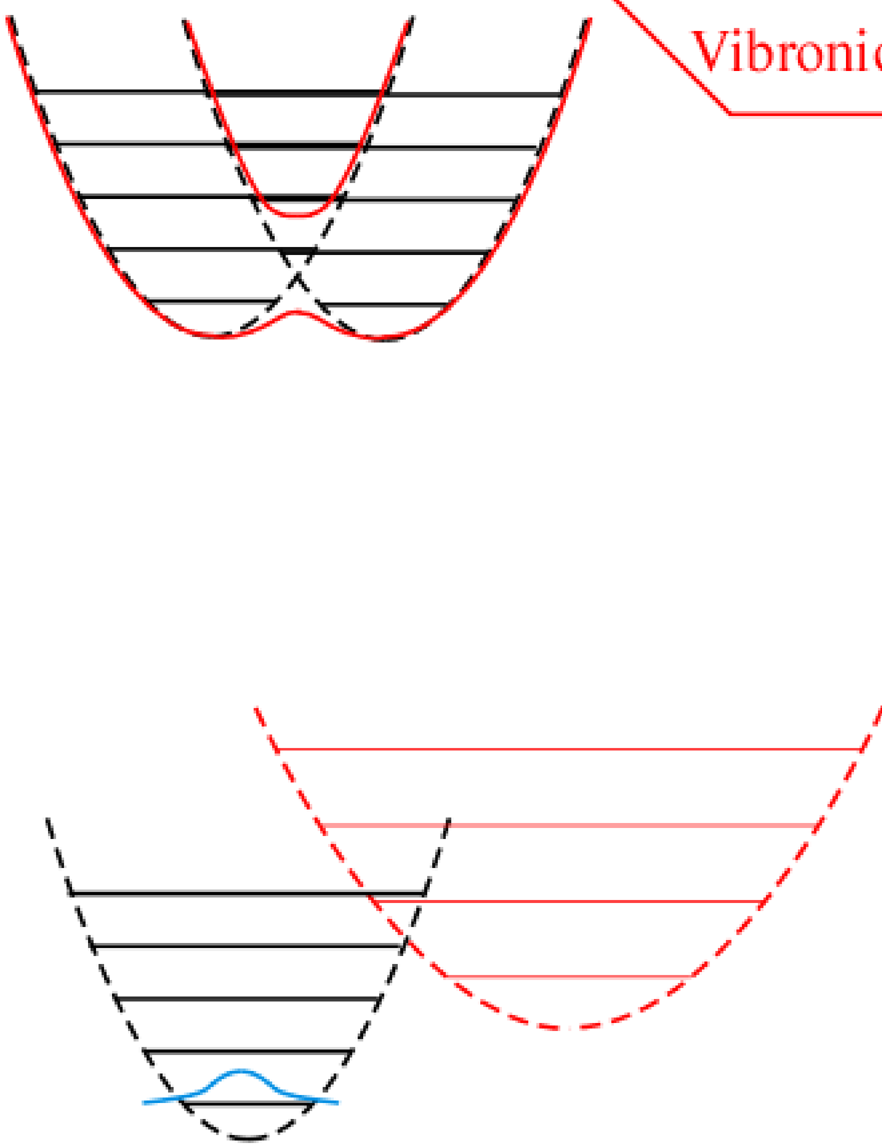
Rotation Energy Eigen-Surfaces (REES)

Inter-PES electronic transitions

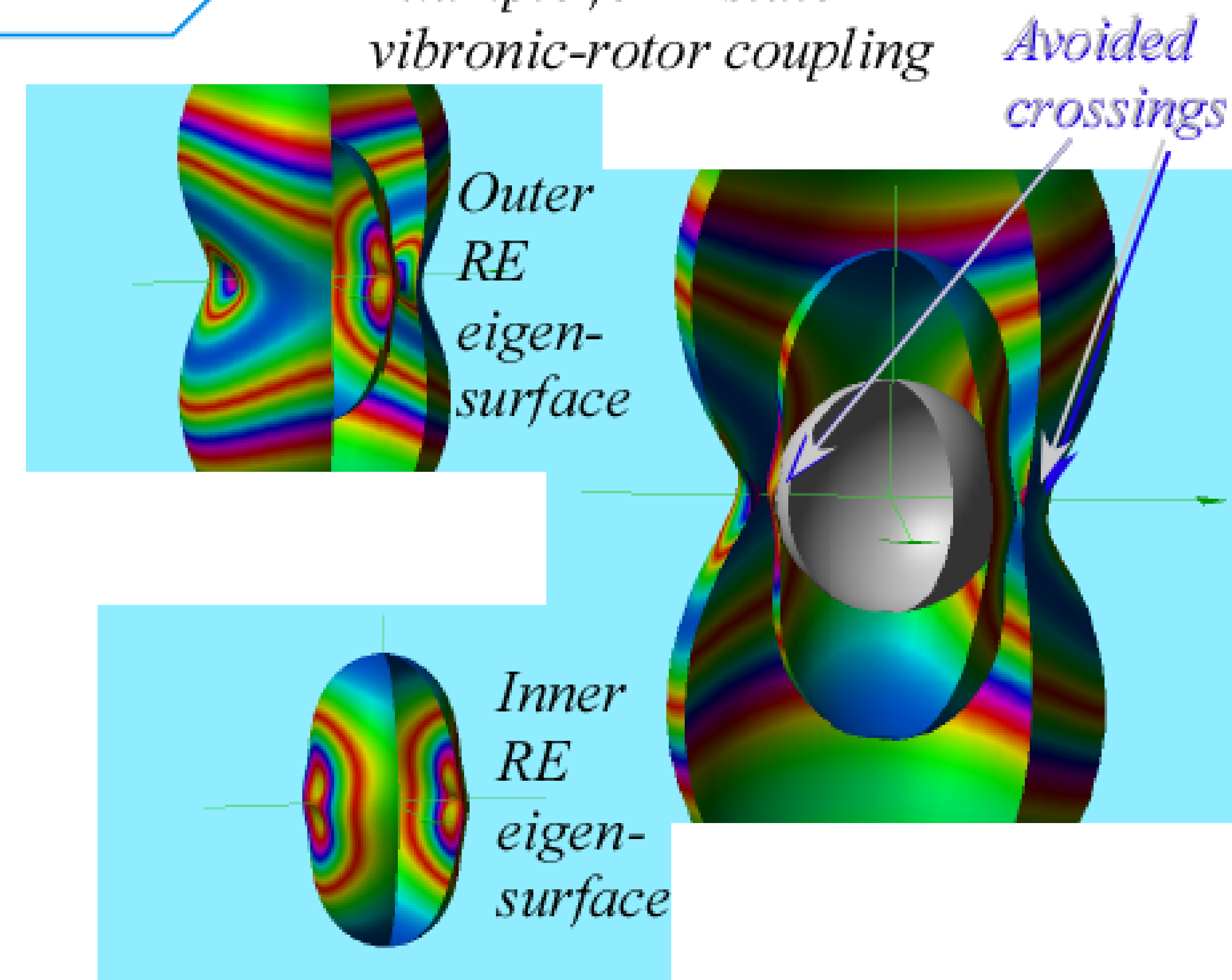
Rotational JTR effects

- Multiple and variable J-axes

Analogy between Vibronic and Rovibronic



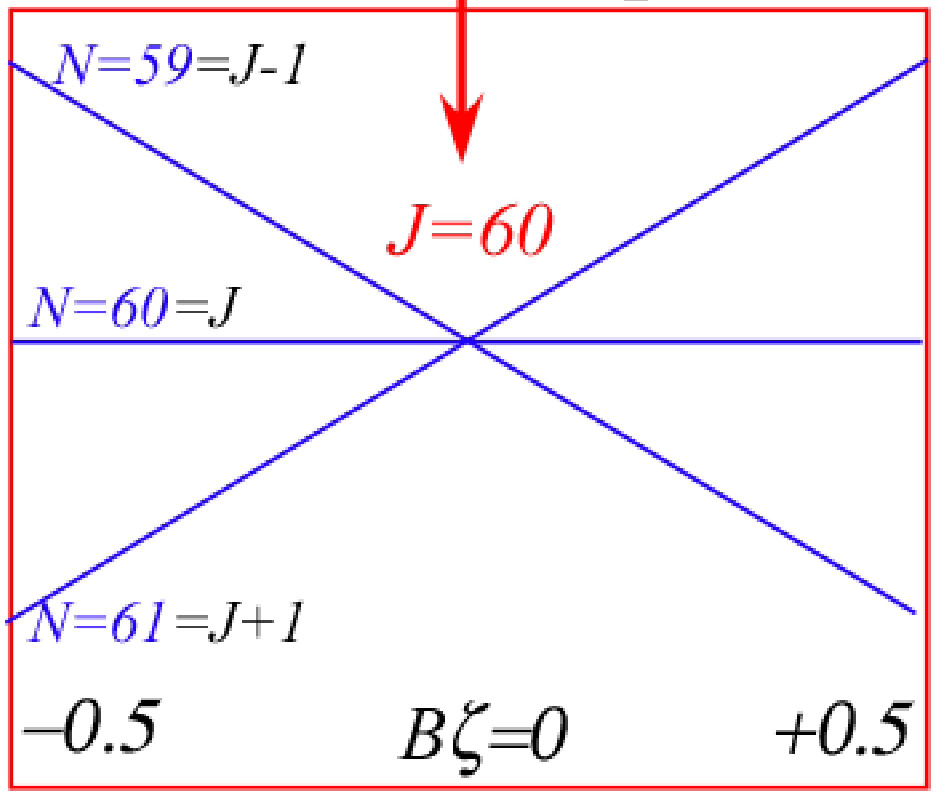
Example for 2-state vibronic-rotor coupling



Recall scalar Coriolis

PQR plots vs. $B\zeta$

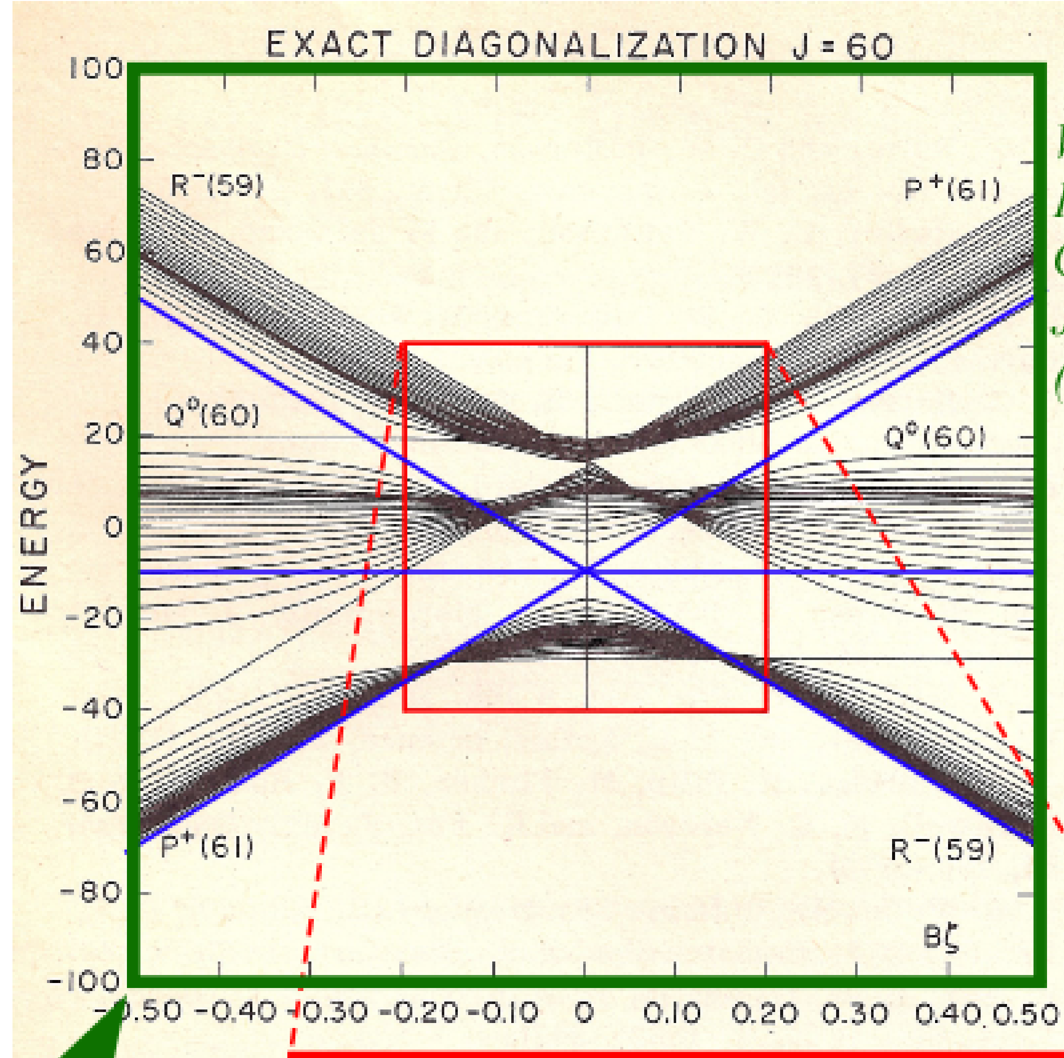
Here is a *J=60* piece of it:



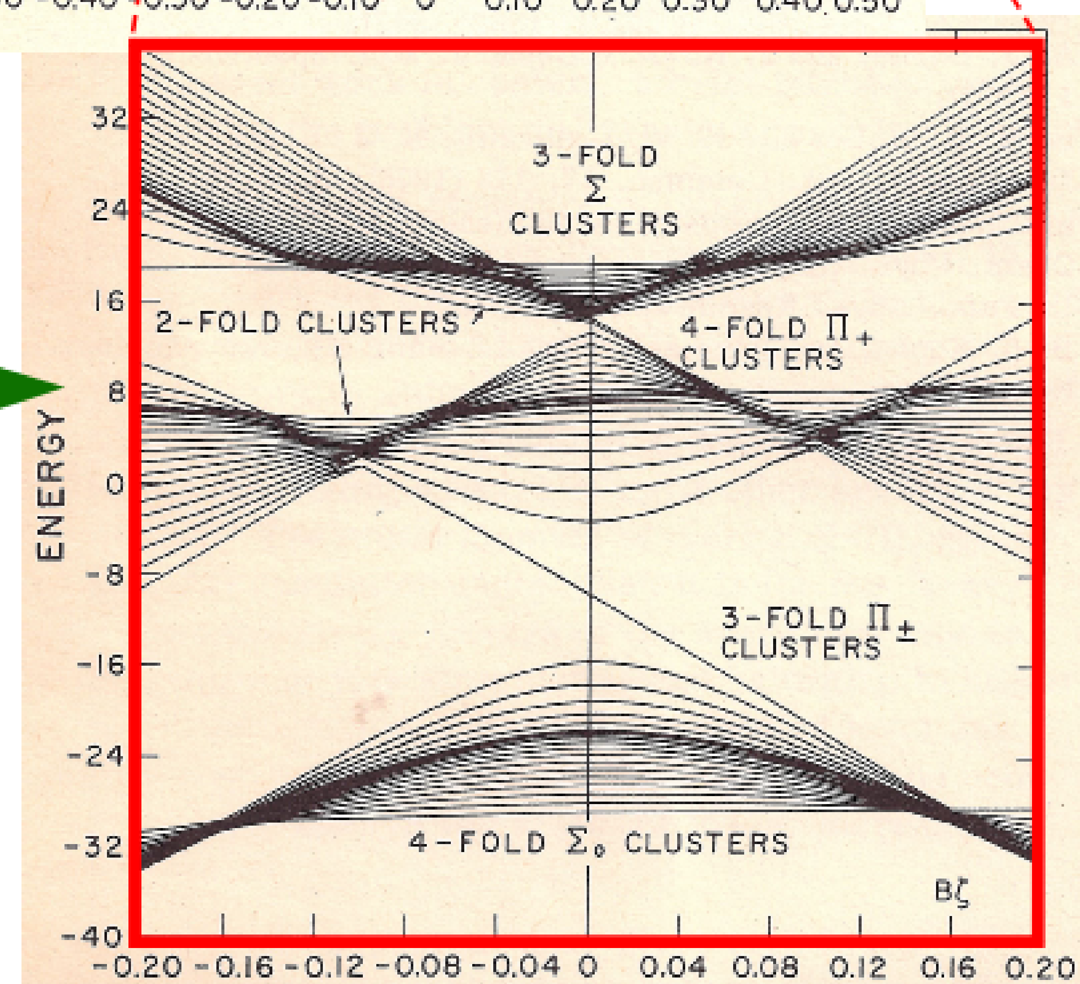
Now consider this plot with *tensor* Coriolis, too.

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

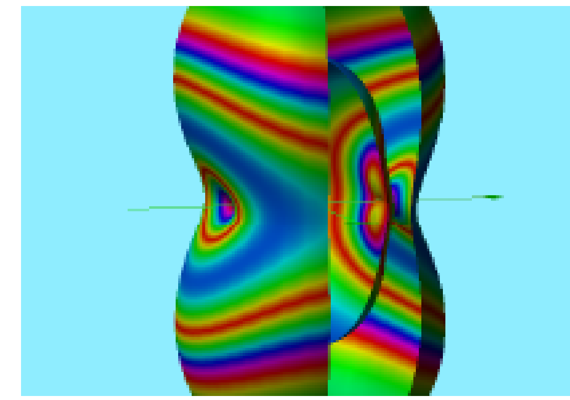
See next talk **RJ06** and a 4PM talk **RI09** by ***Mitchell et. al.*** and ***Boudon et. al.*** who will pull much higher rank!)



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

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

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

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

Lab-PQR-Basis

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

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

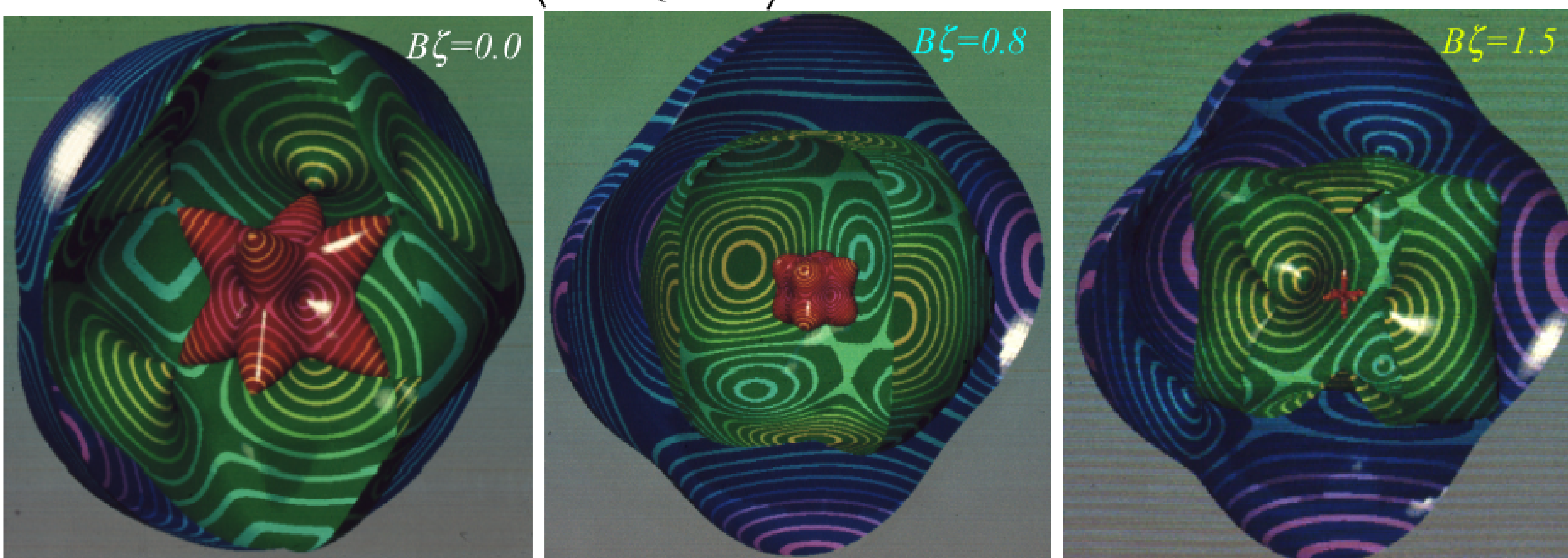
$$+2t_{224}|J|^2\begin{pmatrix}H_{PP}&H_{PQ}&H_{PR}\\H^*_{PQ}&H_{QQ}&H_{QR}\\H^*_{RP}&H^*_{QR}&H_{RR}\end{pmatrix}$$

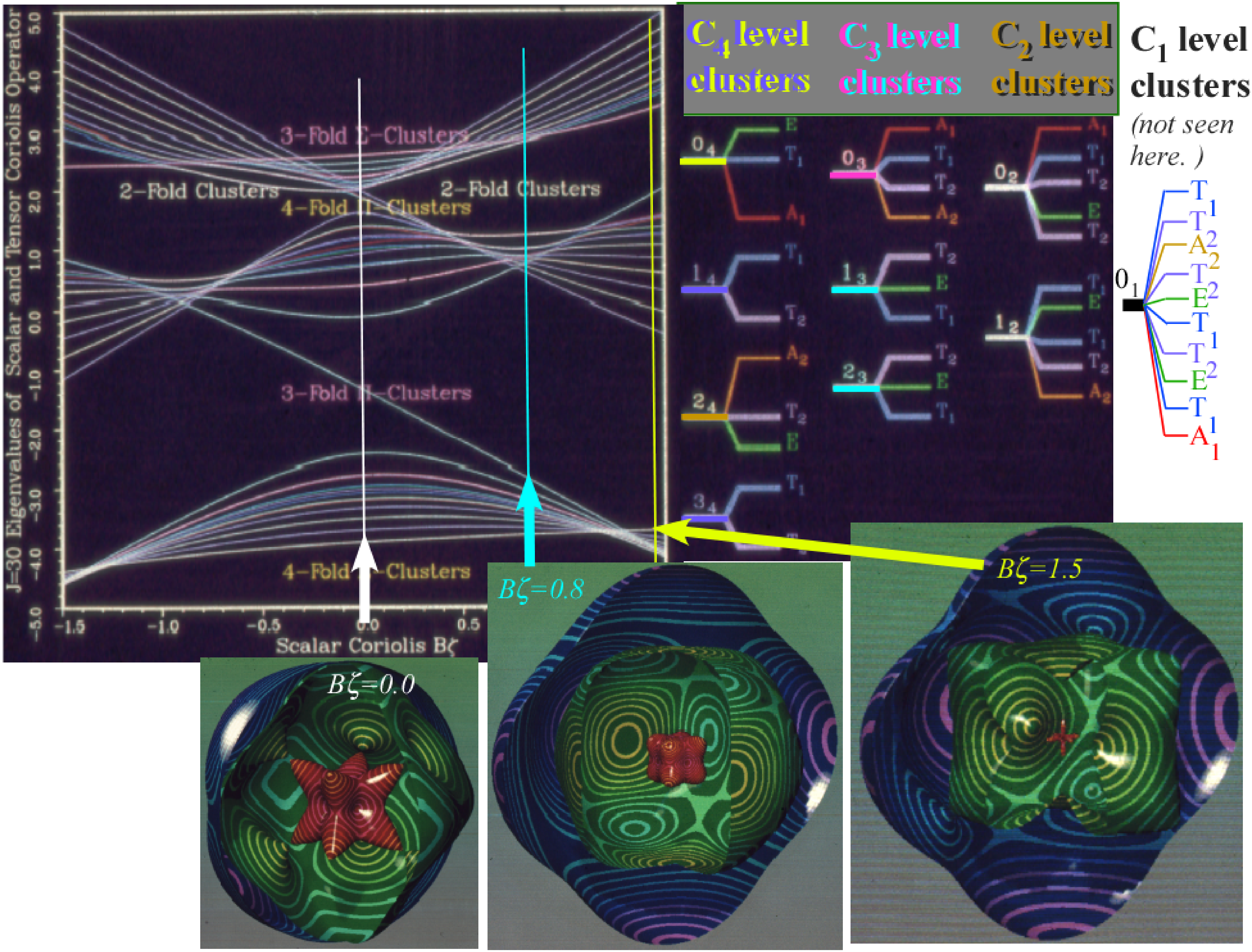
(Either basis should give same REES)

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

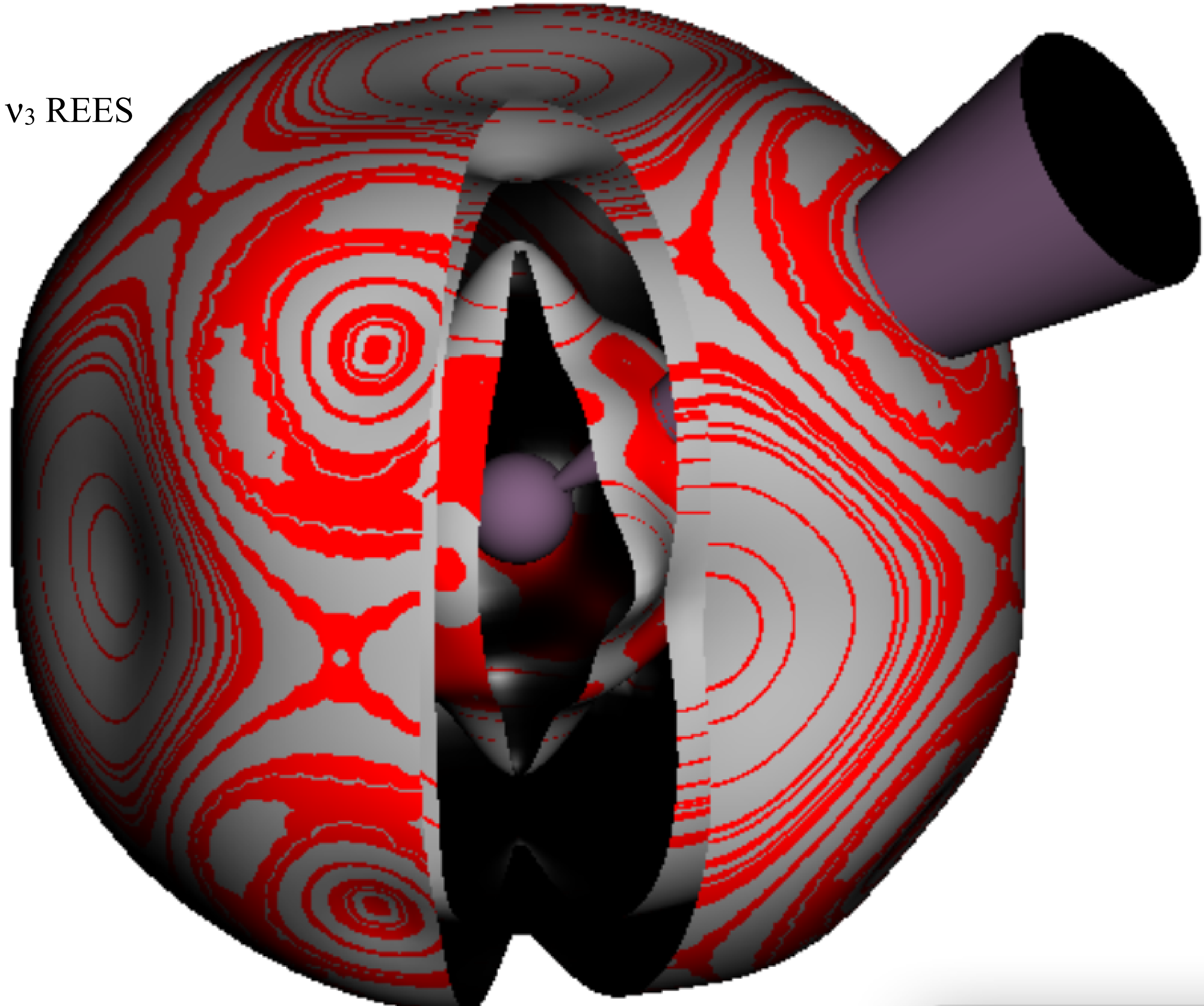
$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

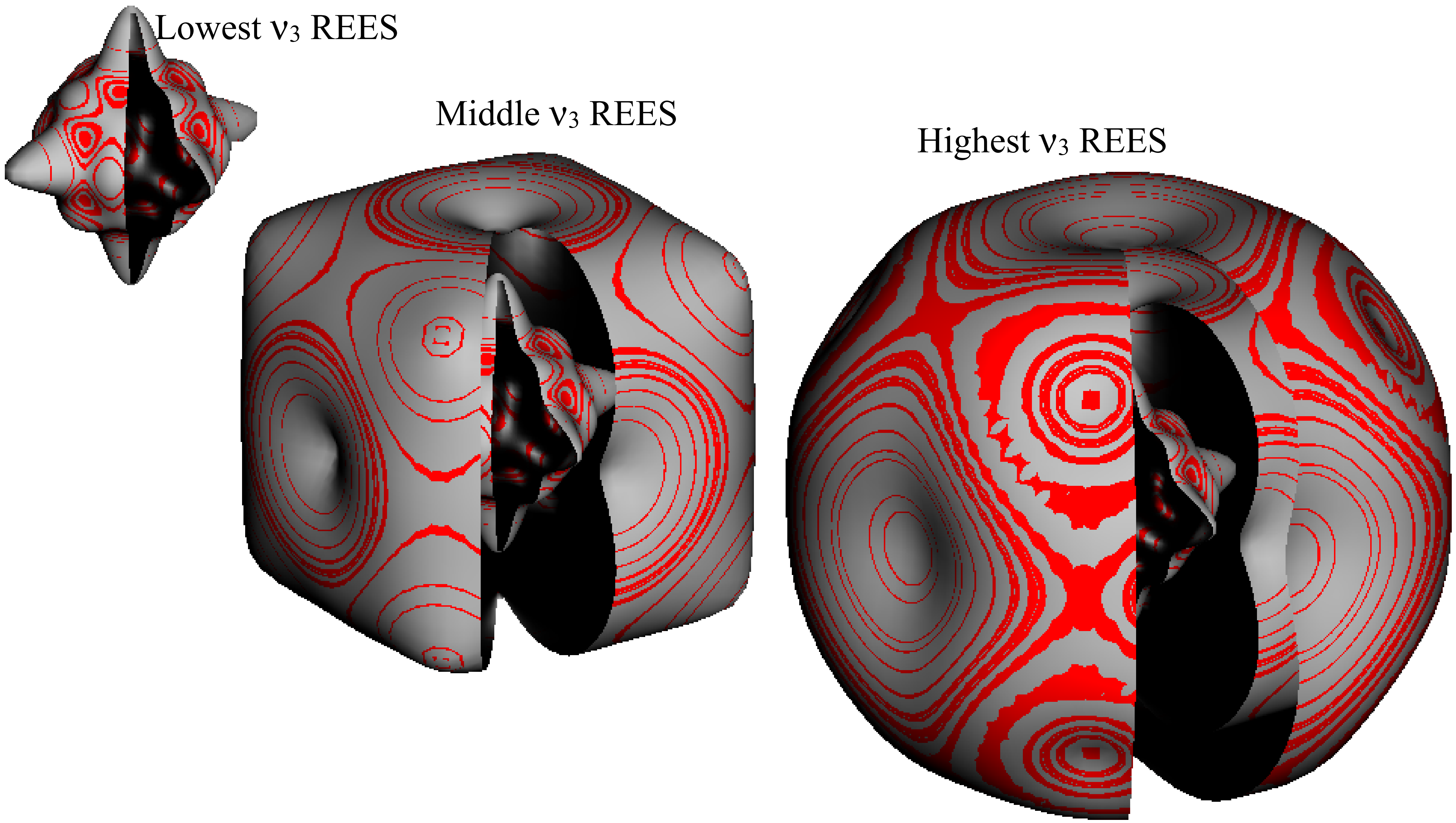
$$H_{PQ}=5(-7\cos^4\beta+8\cos^2\beta+(1-\cos^4\beta)\cos4\gamma+2i\cos\beta\sin^2\beta\sin4\gamma-1)/4$$





J=30 Eigenvalues of Scalar and Tensor Coriolis Operator
Scalar Coriolis Bζ
3-Fold E-Clusters
2-Fold Clusters
2-Fold Clusters
4-Fold II-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 ν3 REES
Middle ν3 REES
Highest ν3 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

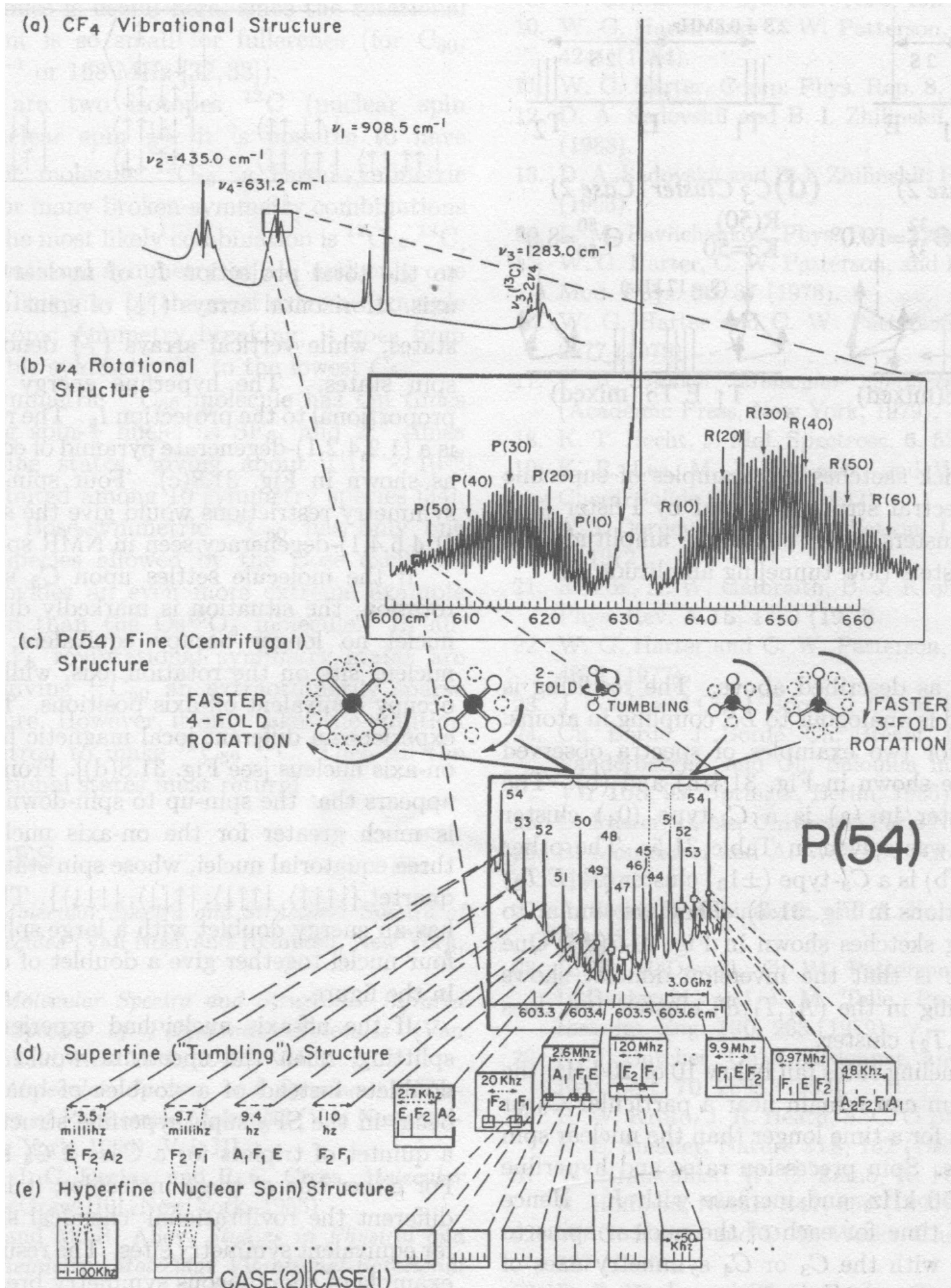
Spherical rotor levels and RES plots

SF_6 spectral fine structure

➔ *CF_4 spectral fine structure*

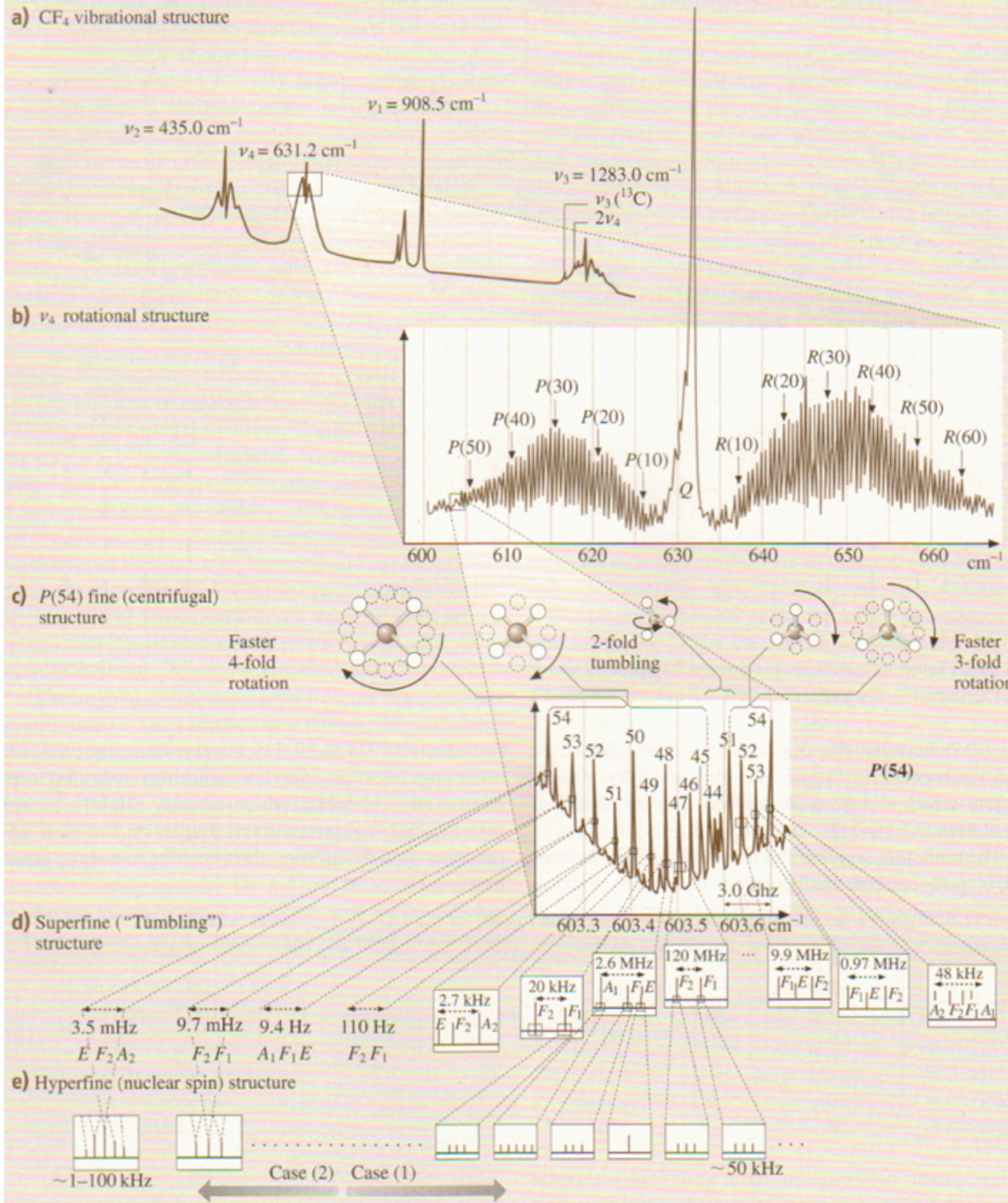
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

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