AMOP Lecture 17
Thur. 4.15 2014

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

Introduction to Rotational Eigenstates and Spectra III

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

Review: 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*
Review: Symmetric rotor levels and RES plots
- *Asymmetric rotor levels and RES plots*
  - *$D_2 \supset C_2$ symmetry correlation*
- *Spherical rotor levels and RES plots*
  - *Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...*
  - *$O \supset C_4$ and $O \supset C_3$ symmetry correlation*
- *Details of P(88) ν_4 SF_6 spectral structure and implications*
  - *Beginning theory*
  - *Rovibronic nomograms and PQR structure*
  - *Rovibronic energy surfaces (RES) and cone geometry*
  - *Spin symmetry correlation, tunneling, and entanglement*
  - *Analogy between PE surface dynamics and RES*
  - *Rotational Energy Eigenvalue Surfaces (REES)*

➡ *Review: 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*

- *Review: Symmetric rotor levels and RES plots*
  - *Asymmetric rotor levels and RES plots*
    - $D_2 \supset C_2$ *symmetry correlation*
  - *Spherical rotor levels and RES plots*
    - *Spectral fine structure of* SF_6, SiF_4, C_8H_8, CF_4,...
    - $O \supset C_4$ *and* $O \supset C_3$ *symmetry correlation*
    - *Details of P(88)* v_4 SF_6 *spectral structure and implications*

Review of freshman Chemistry and Physics (contd)

Momentum 101 $p = m\,v$ (linear) $J = L = I\,\omega$ (rotation) BANG!

Energy 101 $E = \frac{1}{2} m\,v^2 = p^2/2m$ $E = \frac{1}{2} I\,\omega^2 = J^2/2I$ $BUCK$

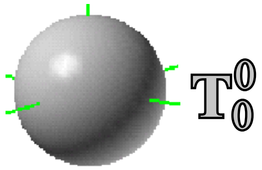
Simple Rigid Rotor Hamiltonian...

(Hamiltonian H=E is $BUCK$ energy in terms of BANG! momentum)

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + \cdots$$

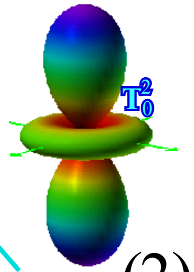
...and its multi-pole expansion...

$$\left(\frac{A+B+C}{3}\right)\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right) + \left(\frac{2C-A-B}{6}\right)\left(2\mathbf{J}_z^2-\mathbf{J}_x^2-\mathbf{J}_y^2\right) + \left(\frac{A-B}{2}\right)\left(\mathbf{J}_x^2-\mathbf{J}_y^2\right)$$



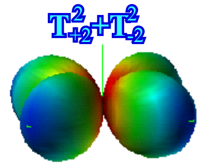
Spherical Top
(A=B=C)
$\mathbf{H} = B\,\mathbf{J}^2$

$$\mathbf{T}_0^{(0)} = \mathbf{J}^2$$



Symmetric Top
(A=B≠C)
$\mathbf{H} = B\,\mathbf{J}^2 + (C - B)(2/3)\mathbf{T}_0^{(2)}$

$$2\mathbf{T}_0^{(2)}$$



$$\sqrt{\frac{2}{3}}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

Asymmetric Top
(A≠B≠C)

$$\mathbf{H} = B\,\mathbf{J}^2 + (2C - A - B)/3\ \mathbf{T}_0^{(2)} + (A - B)/\sqrt{6}\left(\mathbf{T}_2^{(2)} + \mathbf{T}_{-2}^{(2)}\right)$$

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*

$$\mathbf{T}^0_0=\mathbf{J}_x{}^2+\mathbf{J}_y{}^2+\mathbf{J}_z{}^2=\mathbf{J}^2$$

$$\mathbf{T}^2_0=\frac{2\mathbf{J}_z{}^2-\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2}=\mathbf{J}^2\frac{3\cos^2\theta-1}{2}=\mathbf{J}^2P_2(\cos\theta)$$

$$\mathbf{T}^2_2+\mathbf{T}^2_{-2}=\sqrt{6}\frac{\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2}=\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi$$

$$\mathbf{H}=A\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2$$

$$=(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C)(\mathbf{J}_x{}^2+\mathbf{J}_y{}^2+\mathbf{J}_z{}^2)$$

$$+(\frac{-1}{6}A+\frac{-1}{6}B+\frac{2}{6}C)(-\mathbf{J}_x{}^2-\mathbf{J}_y{}^2+2\mathbf{J}_z{}^2)$$

$$+(\frac{1}{2}A+\frac{-1}{2}B+0\cdot C)(\mathbf{J}_x{}^2-\mathbf{J}_y{}^2+0)$$

$$=(\frac{1}{3}A+\frac{1}{3}B+\frac{1}{3}C)(\mathbf{J}_x{}^2+\mathbf{J}_y{}^2+\mathbf{J}_z{}^2)$$

$$+(\frac{-1}{3}A+\frac{-1}{3}B+\frac{2}{3}C)(\frac{2\mathbf{J}_z{}^2-\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2})$$

$$+(\frac{1}{\sqrt{6}}A+\frac{-1}{\sqrt{6}}B+0\cdot C)(\sqrt{6}\frac{\mathbf{J}_x{}^2-\mathbf{J}_y{}^2}{2})$$

$$=\frac{1}{3}(A+B+C)(\mathbf{T}^0_0)$$

$$+\frac{1}{3}(-A-B+2C)(\mathbf{T}^2_0)$$

$$+\frac{1}{\sqrt{6}}(A-B)(\mathbf{T}^2_2+\mathbf{T}^2_{-2})$$

Resulting asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2=\frac{1}{3}(A+B+C)(\mathbf{T}^0_0)+\frac{1}{3}(2C-A-B)(\mathbf{T}^2_0)+\frac{A-B}{\sqrt{6}}(\mathbf{T}^2_2+\mathbf{T}^2_{-2})$$

Resulting semi-classical asymmetric top Hamiltonian expansion:

asymmetry term

$$\mathbf{H}=A\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2=\frac{1}{3}(A+B+C)(\mathbf{J}^2)+\frac{1}{3}(2C-A-B)(\mathbf{J}^2\frac{3\cos^2\theta-1}{2})+\frac{A-B}{\sqrt{6}}(\sqrt{\frac{3}{2}}\mathbf{J}^2\sin^2\theta\cos 2\phi)$$

$$\mathbf{H}=A\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2=\mathbf{J}^2\left[\frac{A+B+C}{3}+\frac{2C-A-B}{6}(3\cos^2\theta-1)+\frac{A-B}{2}\sin^2\theta\cos 2\phi\right]$$

Resulting semi-classical symmetric top Hamiltonian expansion:

$$\mathbf{H}=B\mathbf{J}_x{}^2+B\mathbf{J}_y{}^2+C\mathbf{J}_z{}^2=\mathbf{J}^2\left[\frac{B+B+C}{3}+\frac{2C-B-B}{6}(3\cos^2\theta-1)+\frac{B-B}{2}\sin^2\theta\cos 2\phi\right]=\mathbf{J}^2\left[B+(C-B)\cos^2\theta\right]$$

$$=B\mathbf{J}^2+(C-B)\mathbf{J}_z{}^2=B\mathbf{J}^2+(C-B)\mathbf{J}^2\cos^2\theta$$

Review: 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

➡ Review: Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

$D_2 \supset C_2$ symmetry correlation

Spherical rotor levels and RES plots

Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...

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

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

Rotational Energy Surface (RES):

Plot Hamiltonian $\mathbf{H}=B\mathbf{J}^2+(C-B)\mathbf{J}_z^{\;2}$ radially as $H(\Theta)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta$

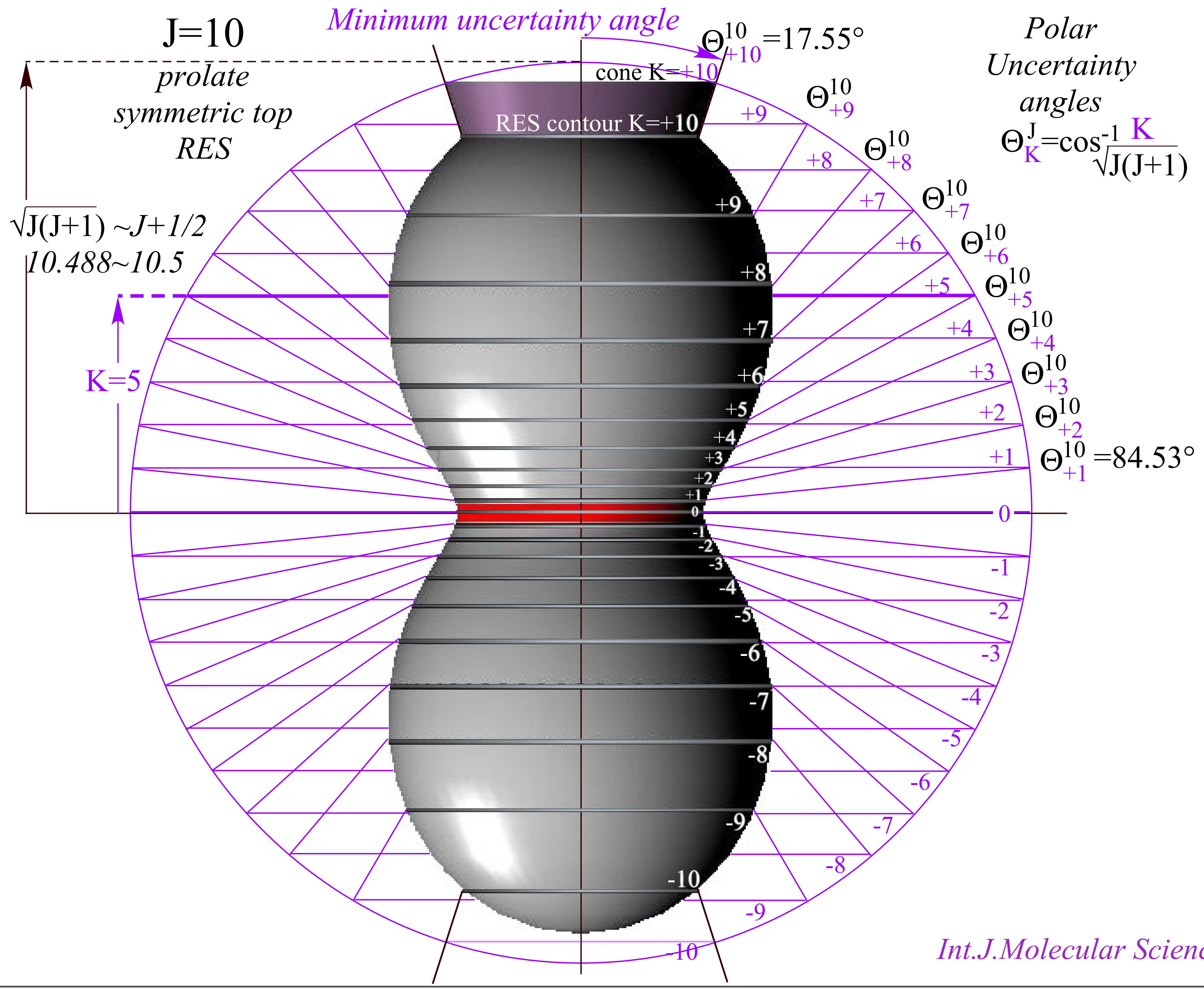
$\left|\begin{matrix} j \\ m,n \end{matrix}\right\rangle$

Conventional notation: n=K

$$H(\Theta_K^J)=BJ(J+1)+(C-B)J(J+1)\cos^2\Theta_K^J$$
$$=BJ(J+1)+(C-B)K^2$$

LAB *BOD*
m=M *n=K*

(Here this gives exact quantum eigenvalues!)



Polar Uncertainty angles

$\Theta^J_K=\cos^{-1}\frac{K}{\sqrt{J(J+1)}}$

Int.J.Molecular Science 14.(2013) Fig.1 p. 730

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Review: Symmetric rotor levels and RES plots

➡ *Asymmetric rotor levels and RES plots*

$D_2\supset C_2$ *symmetry correlation*

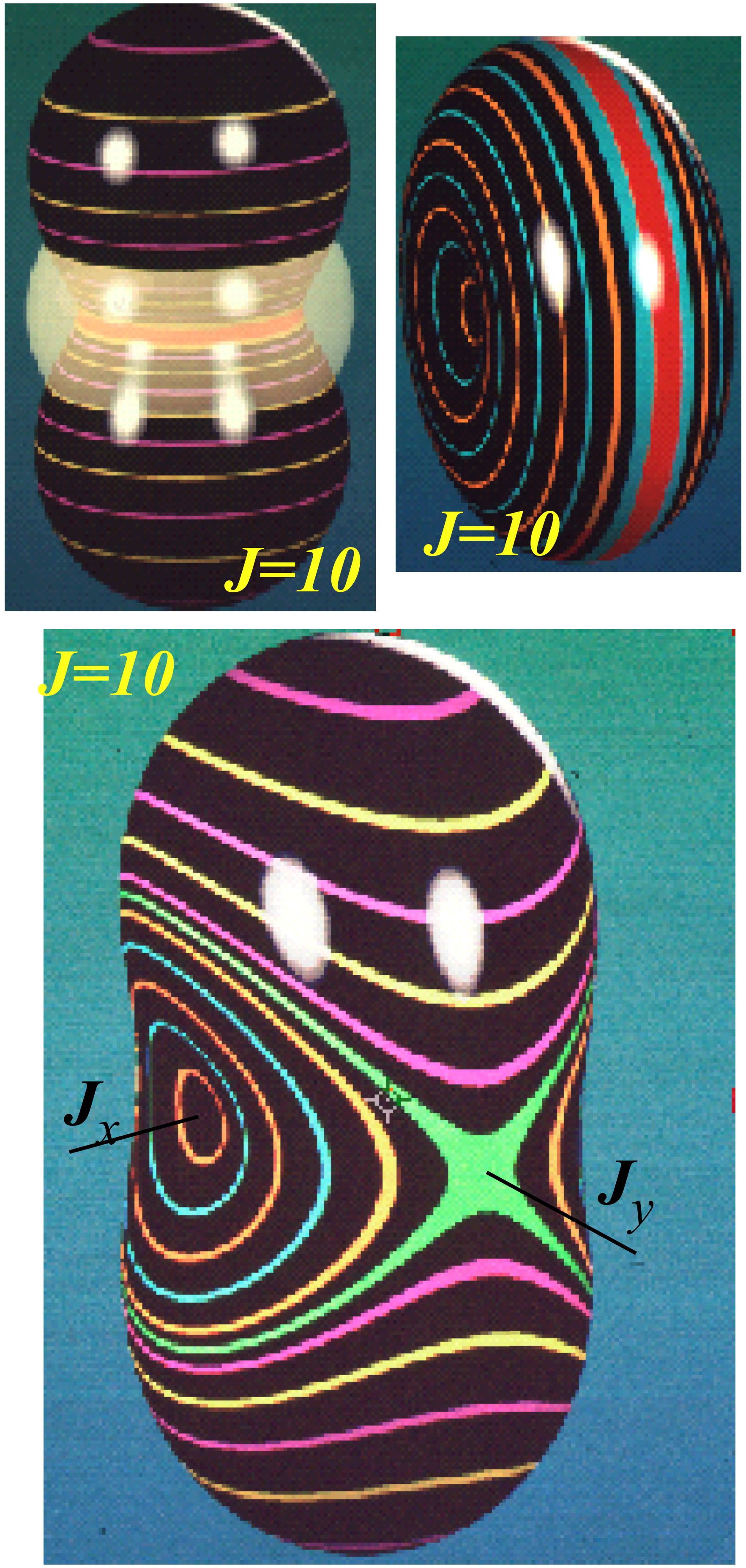
Spherical rotor levels and RES plots

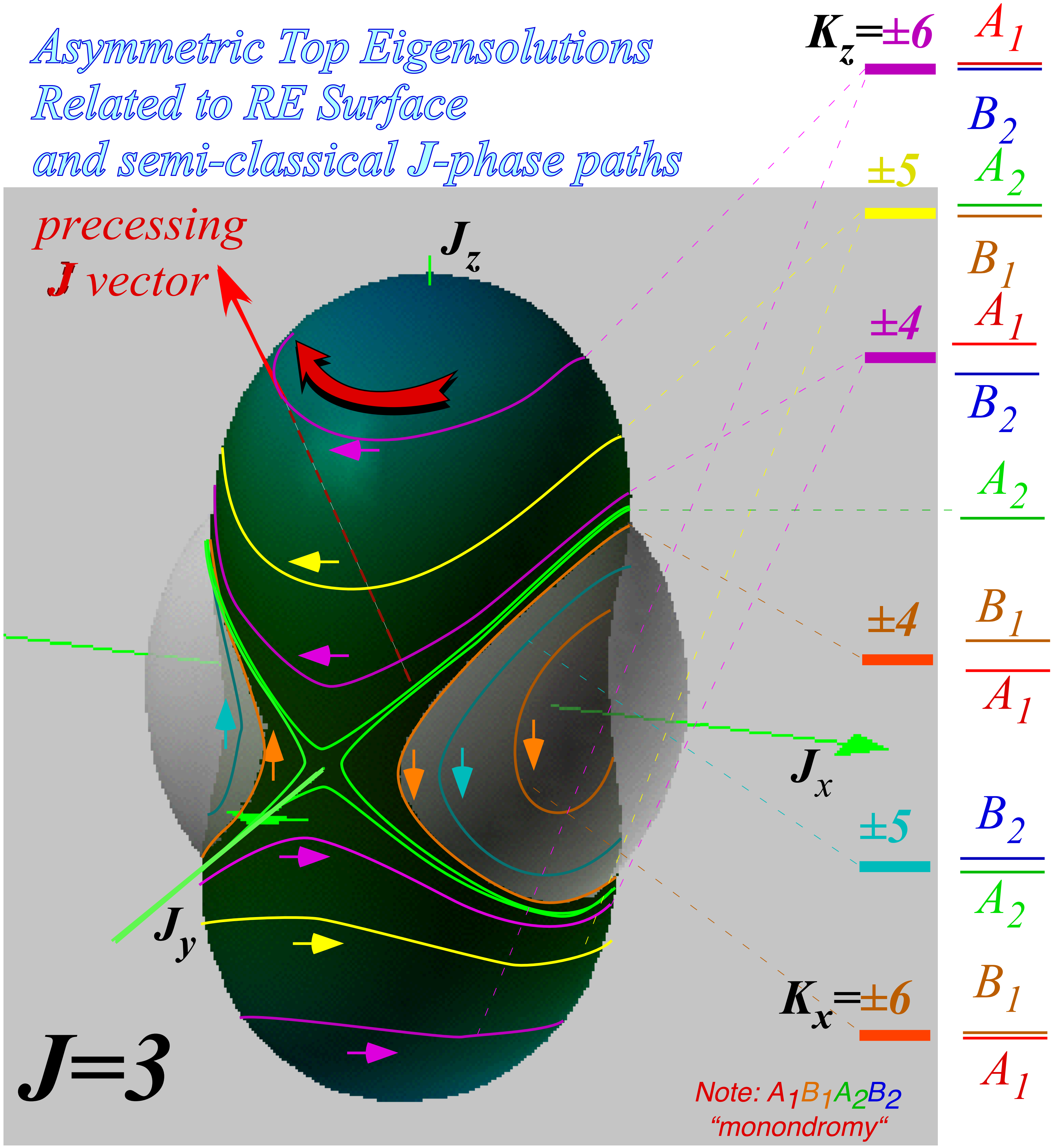
Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...

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

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

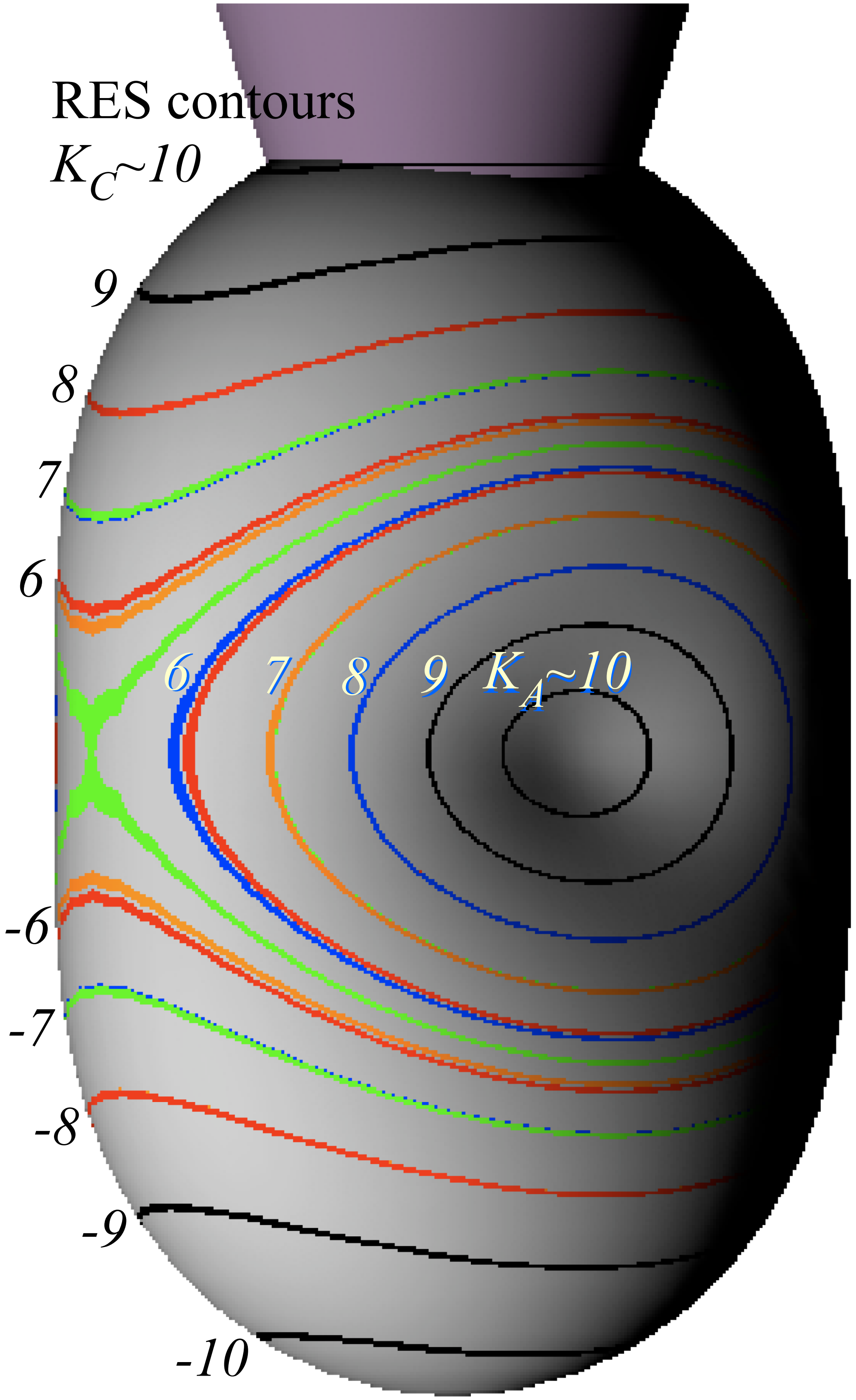
Asymmetric Top Eigensolutions Related to RE Surface and semi-classical J-phase paths





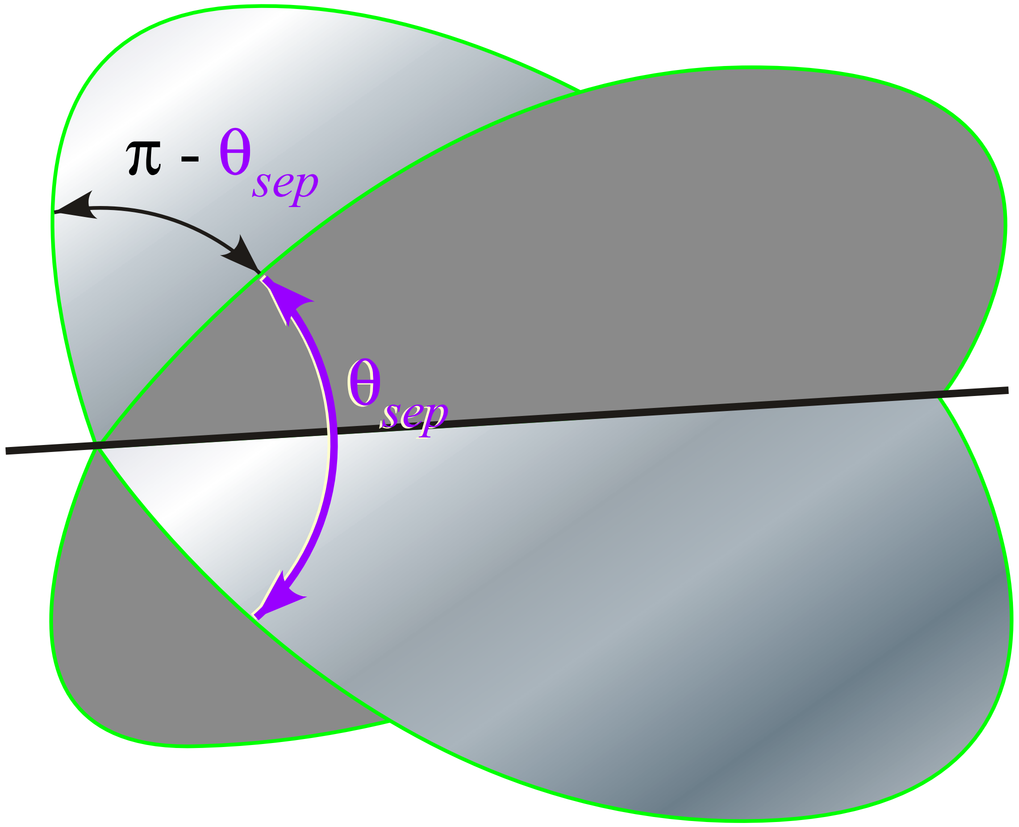
Note: $A_1B_1A_2B_2$ "monondromy"

after QTforCA Unit 8. Ch. 25 Fig. 25.4.1



Separatrix circle pair dihedral angle

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



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

Molecular Symmetry and Dynamics | 32.2 Rotational Energy Surfaces and Semiclassical Rotational Dynamics

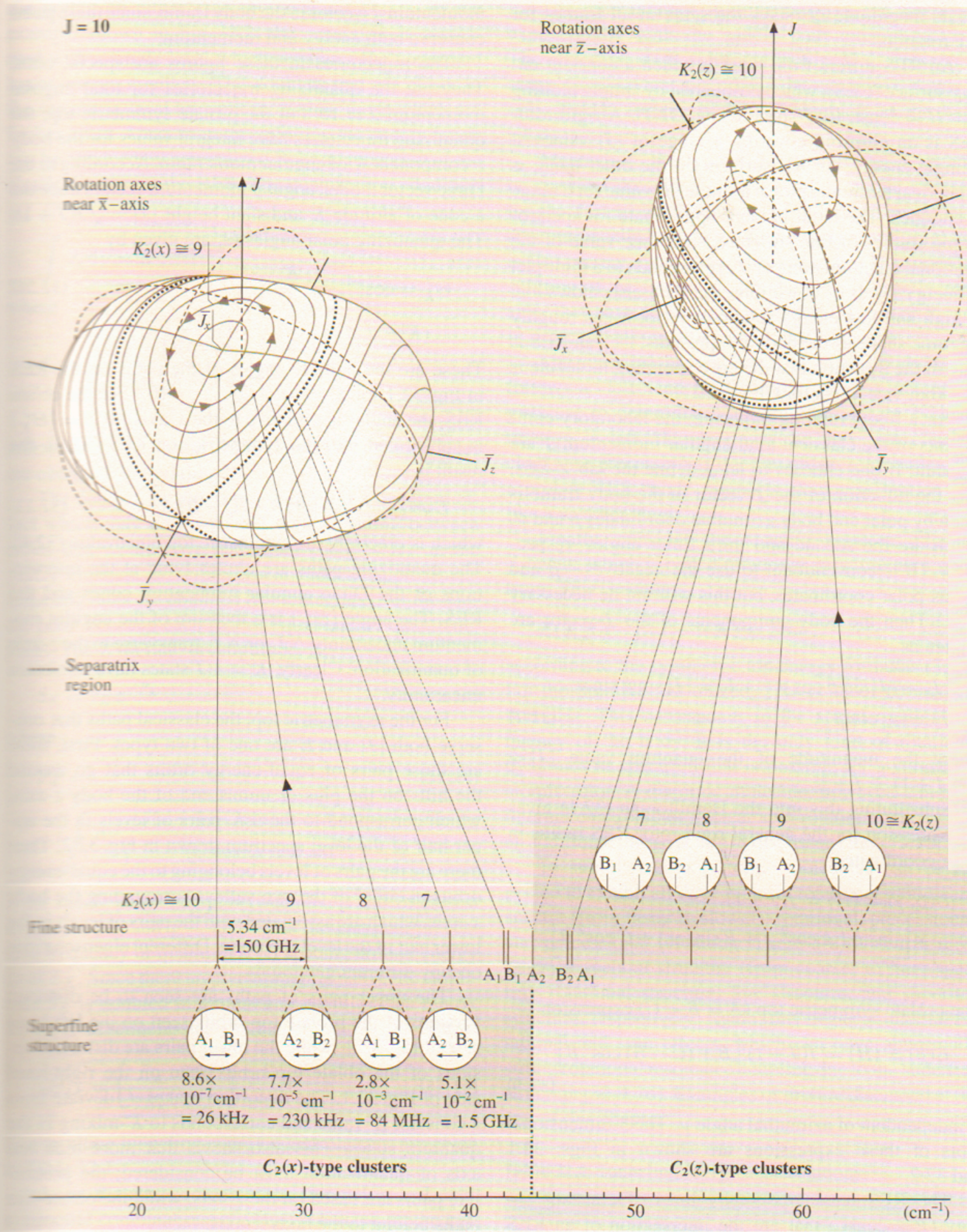
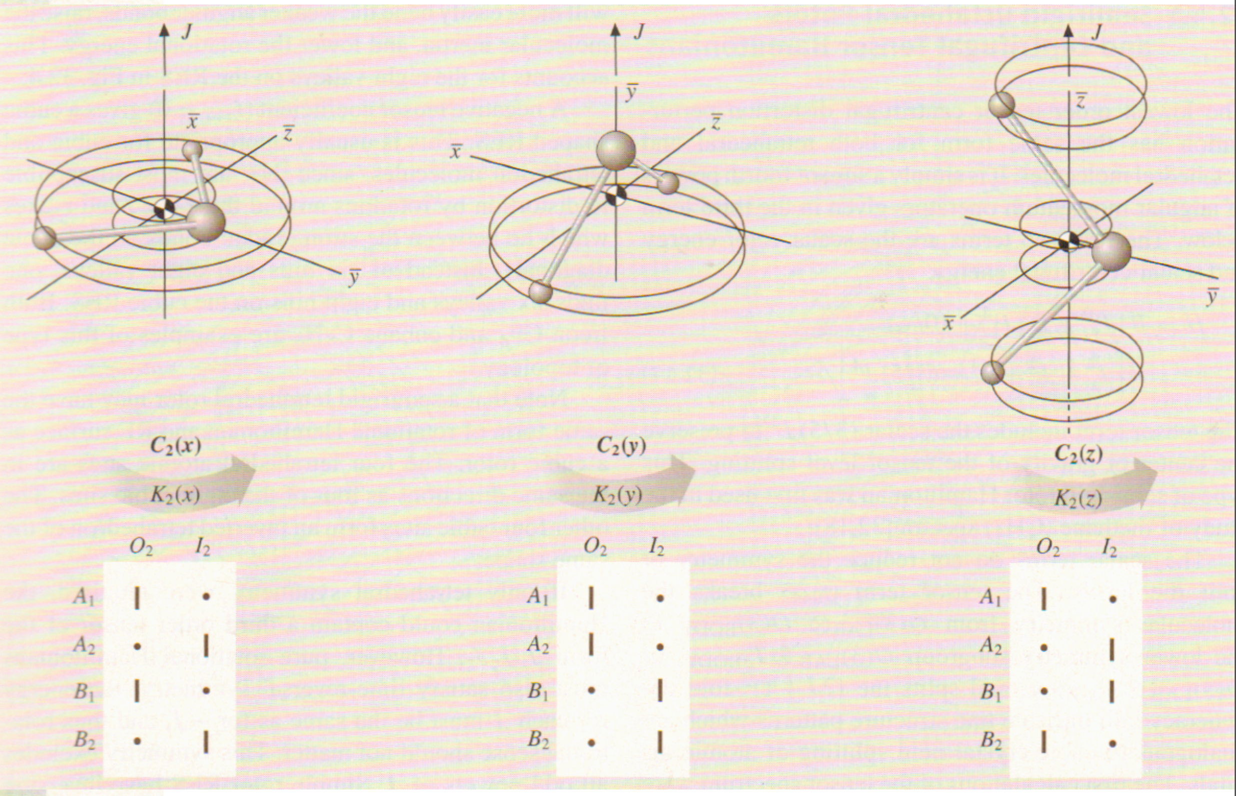


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator $(A = 0.2,\ B = 0.4,\ C = 0.6\,\text{cm}^{-1})$

Examples of Group⊃Sub-group correlation

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



	O_2	I_2
A_1	|	•
A_2	•	|
B_1	|	•
B_2	•	|

	O_2	I_2
A_1	|	•
A_2	|	•
B_1	•	|
B_2	•	|

	O_2	I_2
A_1	|	•
A_2	•	|
B_1	•	|
B_2	|	•

Springer Handbook
of
Atomic, Molecular, and Optical
Physics (2005)
Fig.32.2 and 32.3 p. 495-497

after QTforCA Unit 8. Ch. 25 Fig. 25.4.2

Review: 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*

- *Review: Symmetric rotor levels and RES plots*
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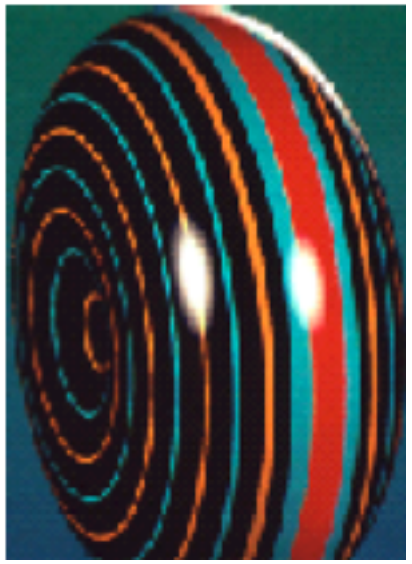
Examples of Group⊃Sub-group correlation

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

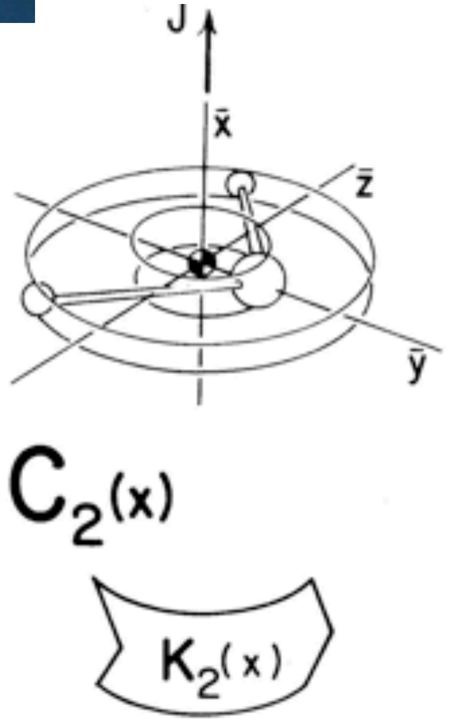
D_2	**1**	$\mathbf{R}_x$	$\mathbf{R}_y$	$\mathbf{R}_z$
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

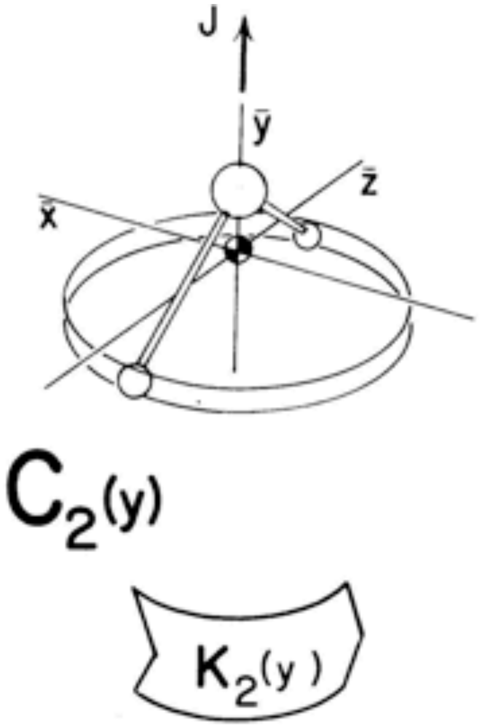


C_{2x}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	1	·
B_2	·	1

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	·





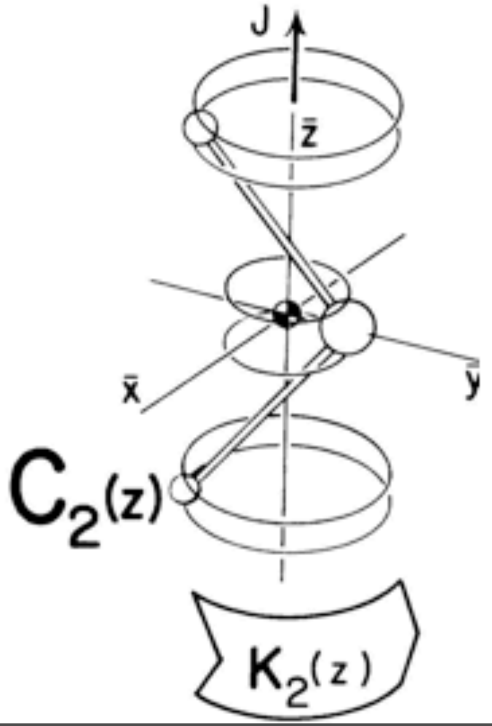
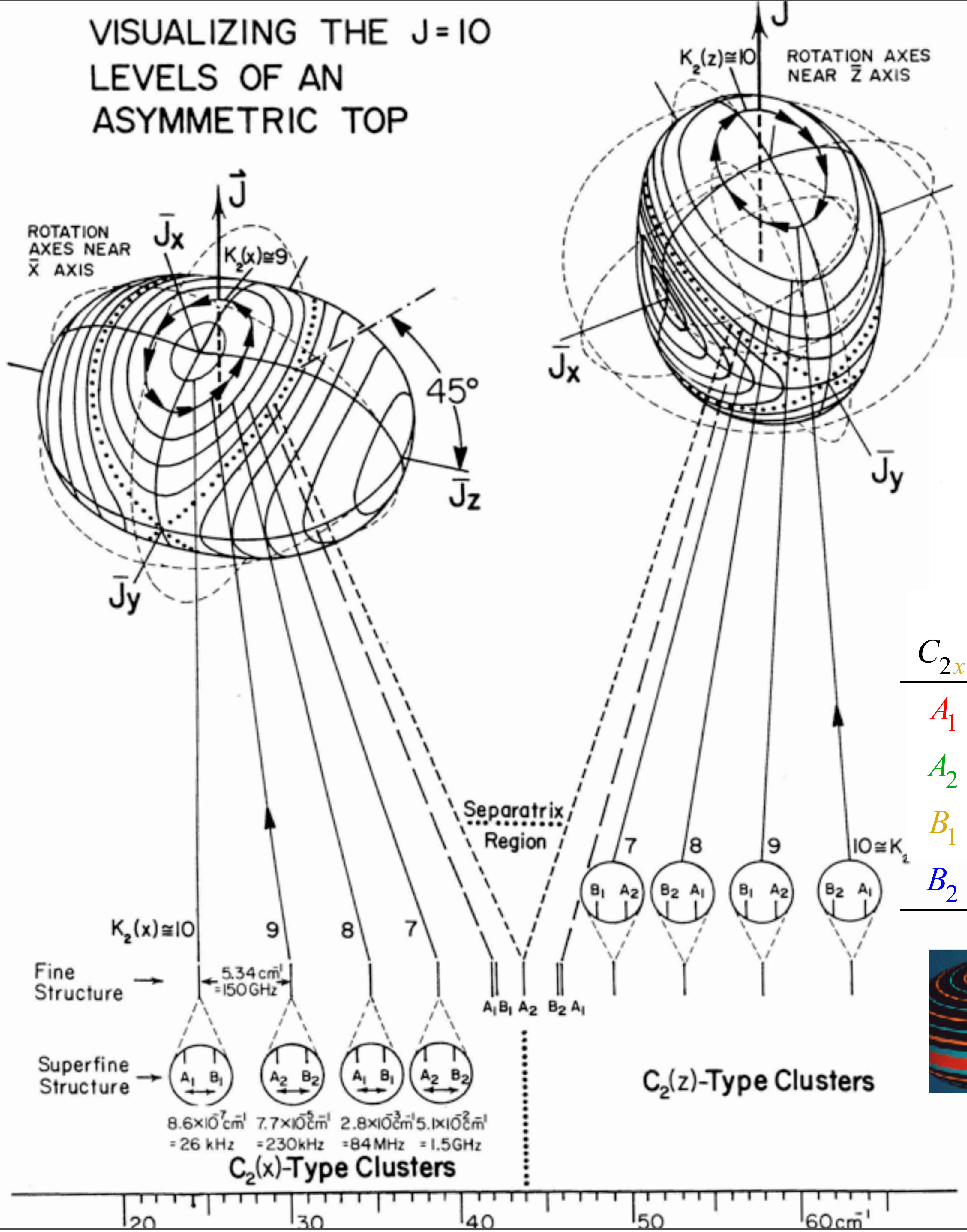


Fig. 25.4.3 *Correlations between the asymmetric top symmetry D_2 and subgroups $C_2(x)$, $C_2(y)$, and $C_2(z)$.*

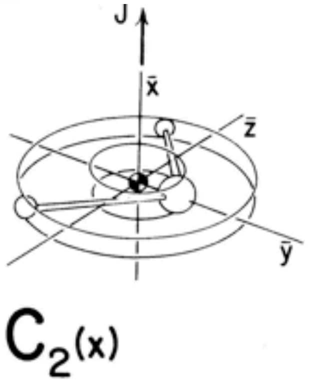
VISUALIZING THE J=10 LEVELS OF AN ASYMMETRIC TOP

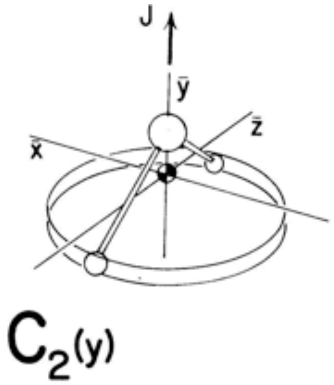


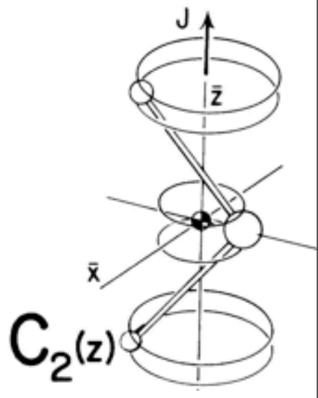
D_2	1	R_x	R_y	R_z
A_1	1	1	1	1
A_2	1	-1	1	−1
B_1	1	1	-1	−1
B_2	1	-1	-1	1

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	·

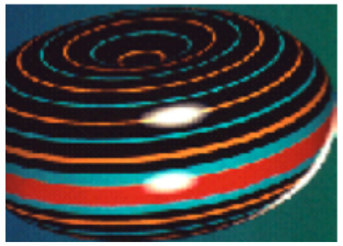


Fig. 25.4.2 *$J = 10$ asymmetric top energy levels and related RE surface paths ($A = 0.2$, $B = 0.4$, $C = 0.6$). Clustered pairs of levels are indicated in magnifying circles that show superfine splittings.*

Molecular Symmetry and Dynamics | 32.2 Rotational Energy Surfaces and Semiclassical Rotational Dynamics

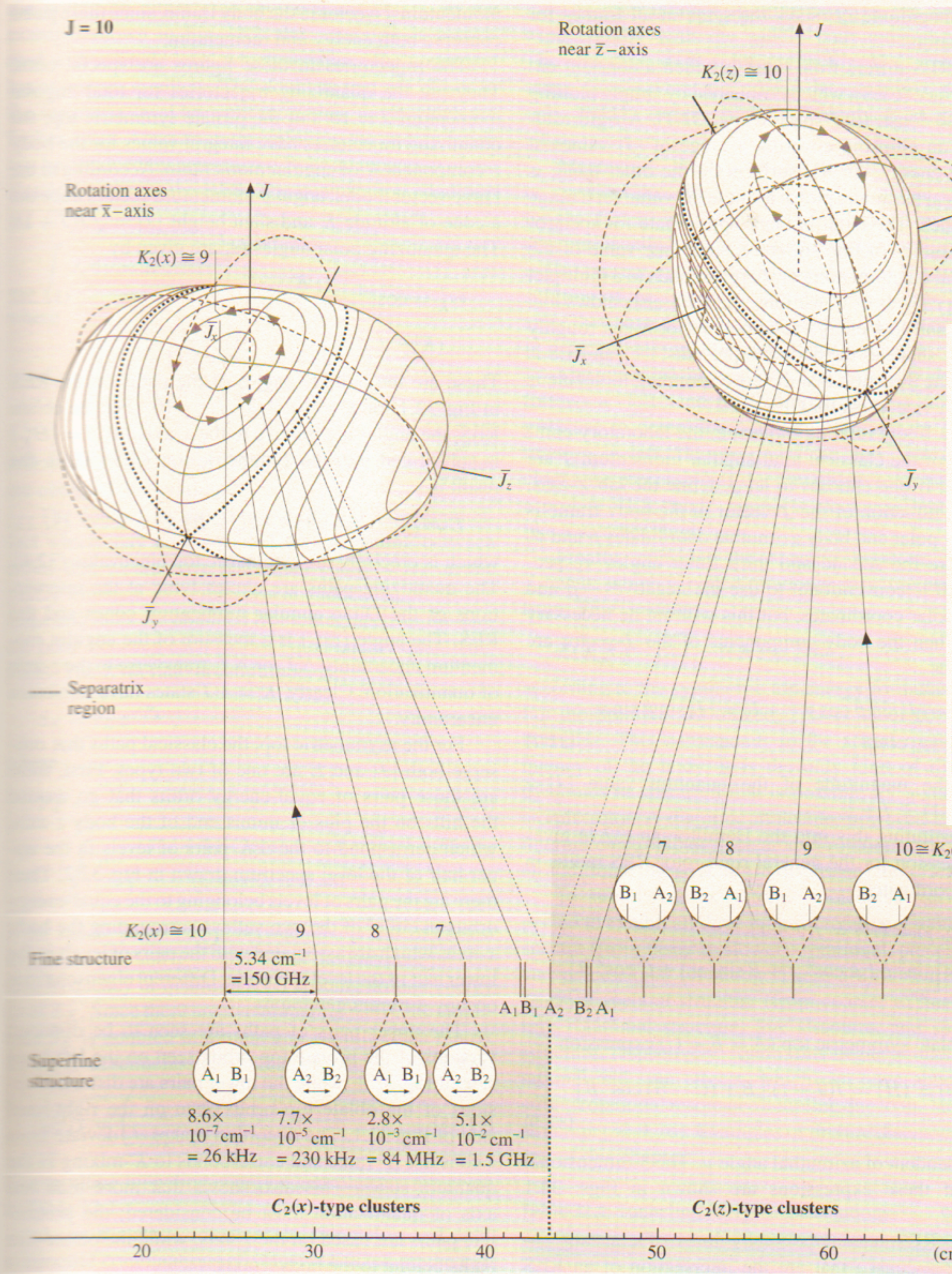


Fig. 32.2 $J = 10$ rotational energy surface and related level spectrum for an asymmetric rigid rotator $(A = 0.2,\ B = 0.4,\ C = 0.6\,\mathrm{cm}^{-1})$

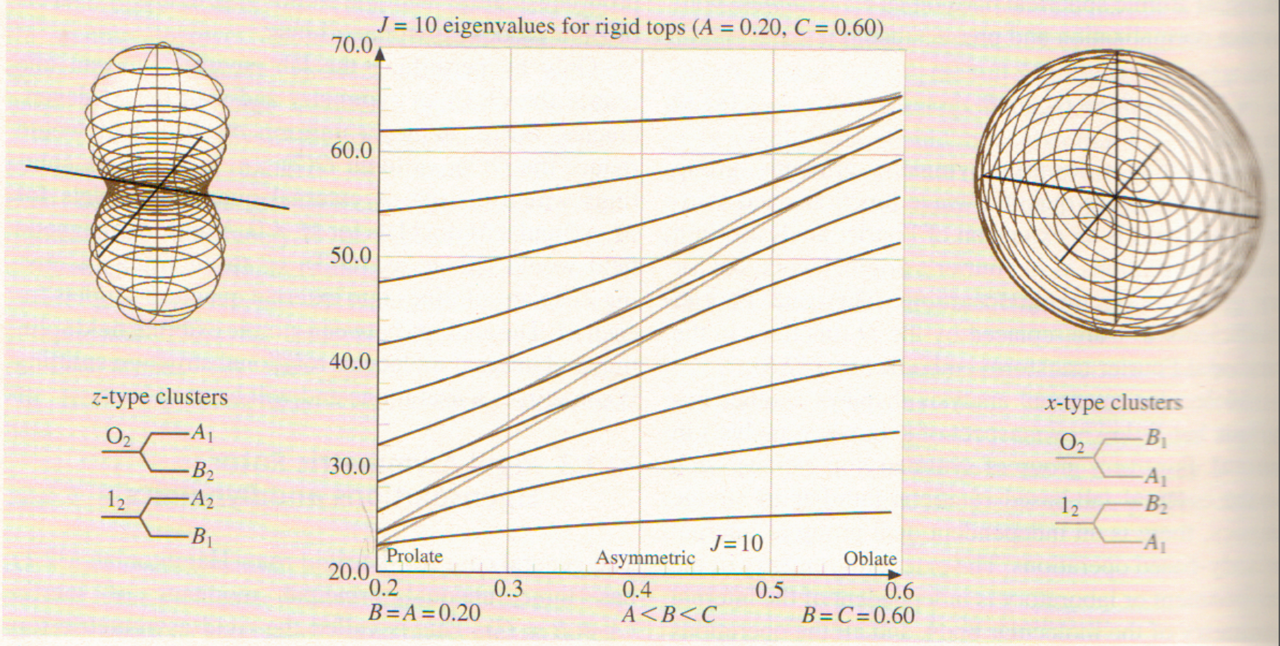


Fig. 32.1 $J = 10$ eigenvalue plot for symmetric rigid rotors. ($A = 0.2$, $C = 0.6\,\mathrm{cm}^{-1}$ $A < B < C$). Prolate and oblate surfaces are shown

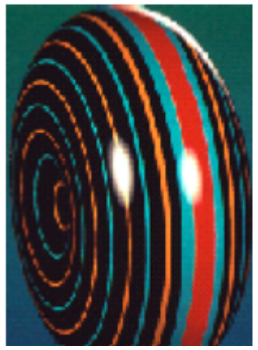
Springer Handbook of Atomic, Molecular, and Optical Physics (2005)

Fig.32.1 and 32.2 p. 494-495

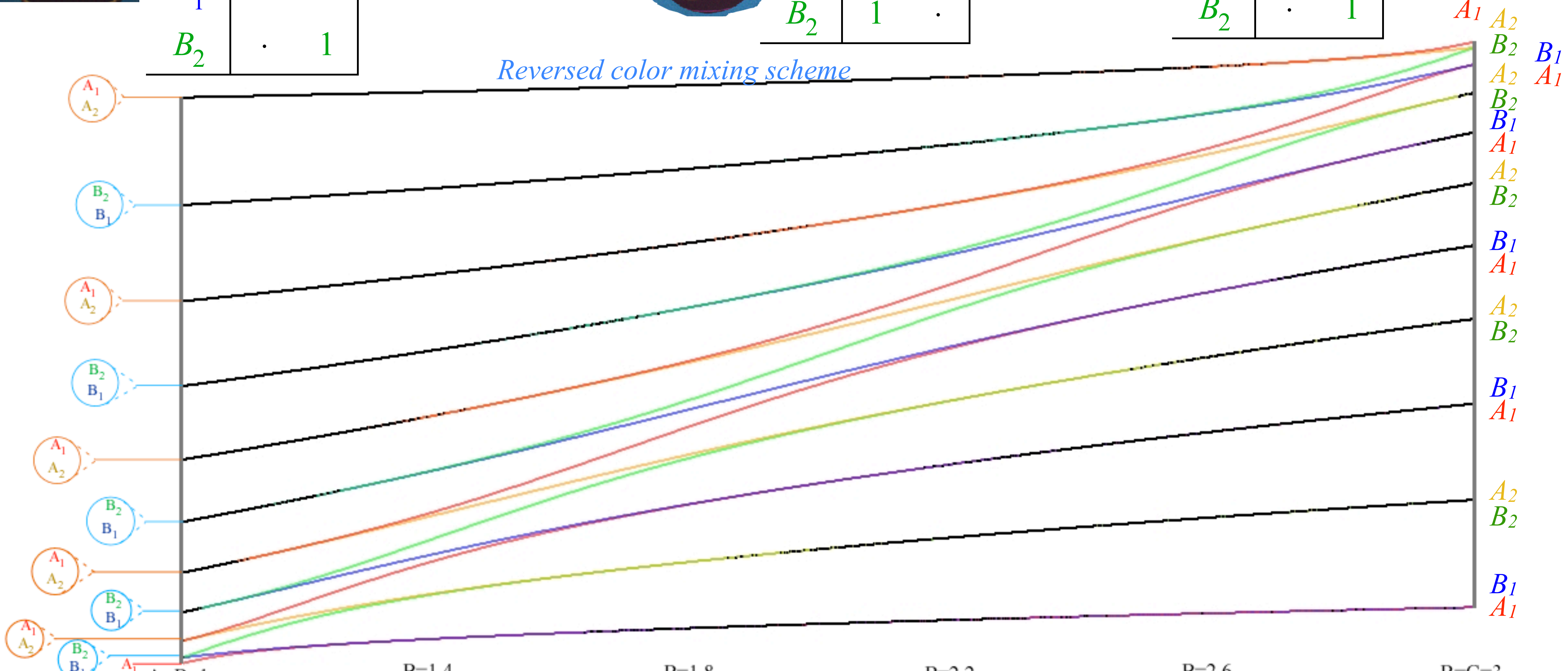
C_{2y}	0_2	1_2
A_1	1	·
A_2	1	·
B_1	·	1
B_2	·	1

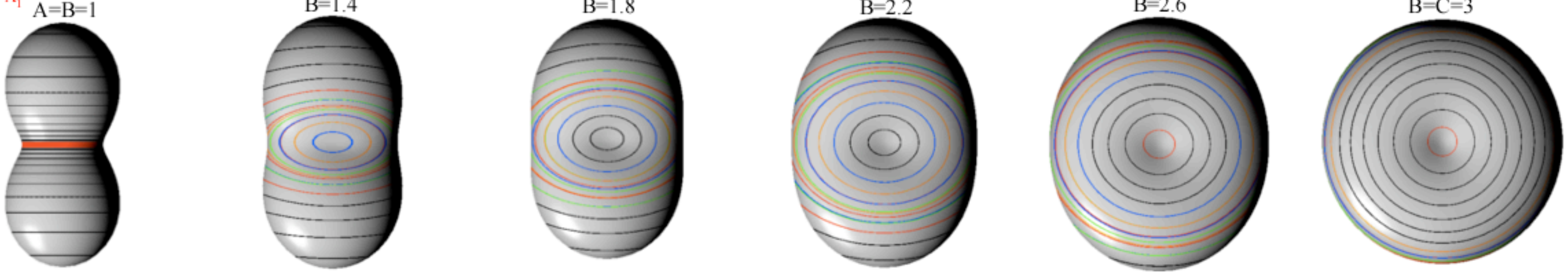
C_{2z}	0_2	1_2
A_1	1	·
A_2	·	1
B_1	·	1
B_2	1	·

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



Reversed color mixing scheme





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

Completing diagonalization from new D_2 basis:

$$\begin{pmatrix} 4C+A+B & \cdot & \cdot & \cdot & \sqrt{3}(A-B) \\ \cdot & 4C+A+B & \cdot & \cdot & \cdot \\ \cdot & \cdot & C+4A+B & \cdot & \cdot \\ \cdot & \cdot & \cdot & C+A+4B & \cdot \\ \sqrt{3}(A-B) & \cdot & \cdot & \cdot & 3A+3B \end{pmatrix}$$

$$\left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_2 2^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle$$

$$\left|B_1 1^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_2 1^-\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+1\end{smallmatrix}\right\rangle - \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-1\end{smallmatrix}\right\rangle$$

$$\left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle$$

Need only diagonalize the two A_1's:

(It is n=0 versus n=2⁺)

$$\begin{pmatrix} 4C+A+B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & 3A+3B \end{pmatrix} \begin{matrix} \left|A_1 2^+\right\rangle = \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\+2\end{smallmatrix}\right\rangle + \tfrac{1}{\sqrt{2}}\left|\begin{smallmatrix}2\\-2\end{smallmatrix}\right\rangle \\ \left|A_1 0\right\rangle = \left|\begin{smallmatrix}2\\0\end{smallmatrix}\right\rangle \end{matrix}$$

$$= (2C+2A+2B)\cdot \mathbf{1} + \begin{pmatrix} 2C-A-B & \sqrt{3}(A-B) \\ \sqrt{3}(A-B) & -(2C-A-B) \end{pmatrix}$$

with eigenvalues:

$$\lambda_\pm = 2C+2A+2B \pm \sqrt{(2C-A-B)^2 + 3(A-B)^2}$$

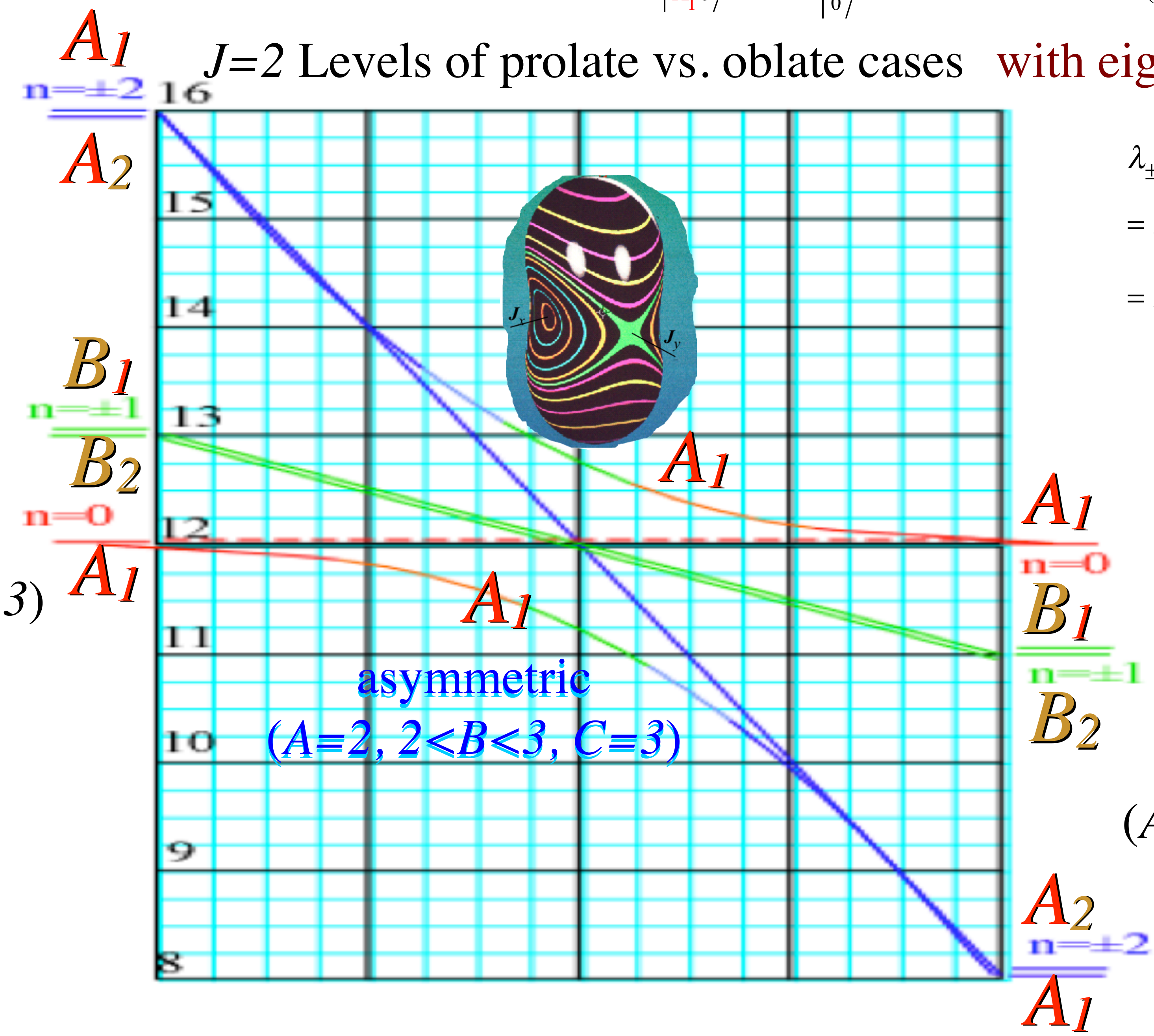
$$= 2(A+B+C) \pm 2\sqrt{C^2-(A+B)C+A^2-AB+B^2}$$

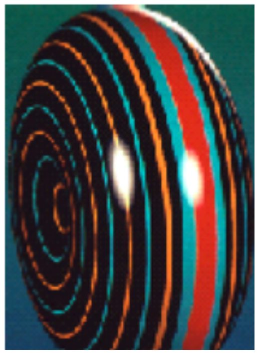
$$= 2C+4B \pm 2(C-B) = \begin{cases} 4C+2B \\ 6B \end{cases} \text{if: } A=B$$

$J=2$ Levels of prolate vs. oblate cases

prolate

($A=2$, $B=2$, $C=3$)





oblate

($A=2$, $B=3$, $C=3$

(Recall (J=2)-example of correlation from Lecture 16)

Review: 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*

Review: Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

$D_2\supset C_2$ *symmetry correlation*

➡ *Spherical rotor levels and RES plots*

Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...

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

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

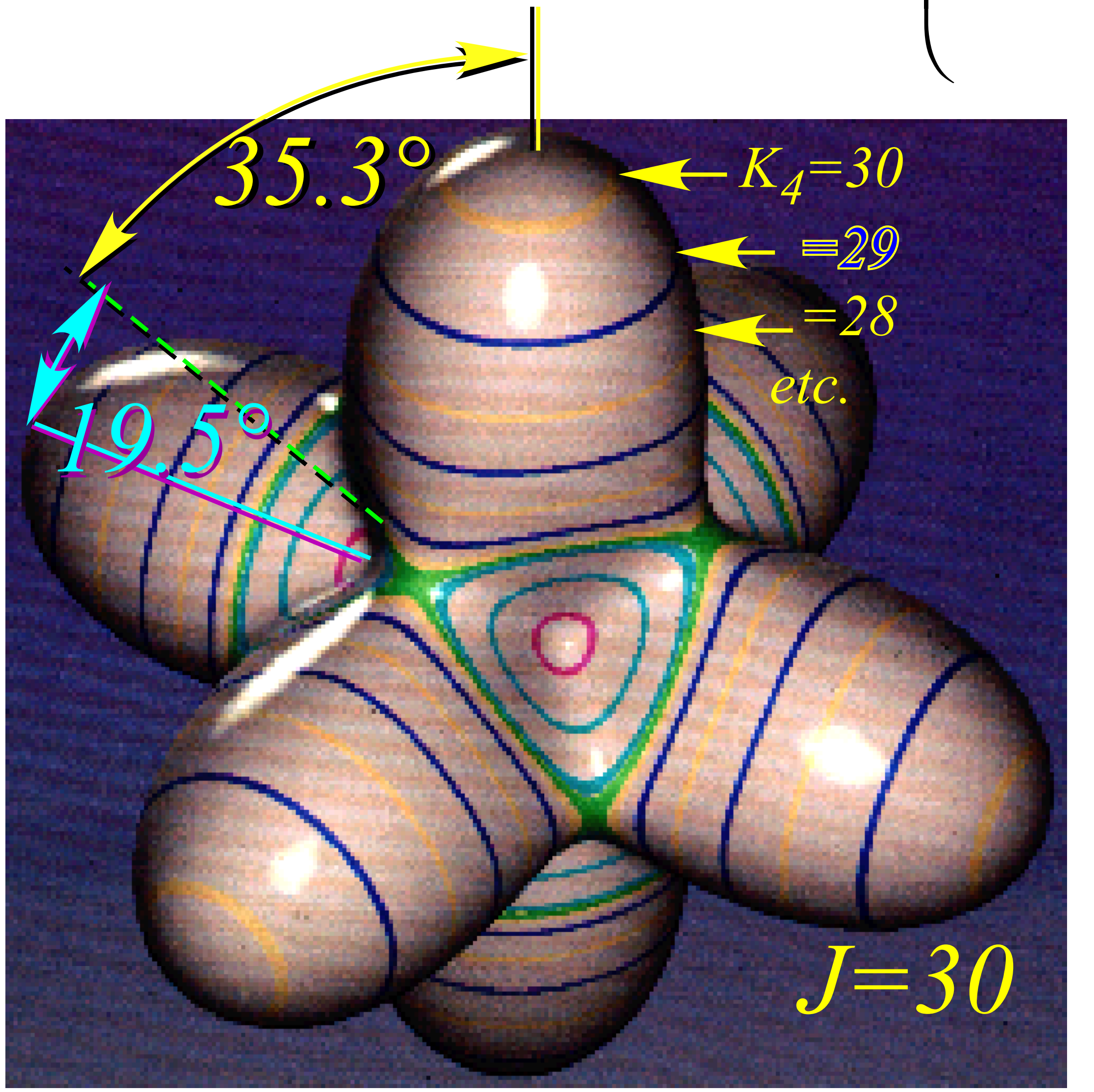
Semi Rigid Rotor Hamiltonian: *Centrifugal and Coriolis terms...*

$$\mathbf{H} = A\mathbf{J}_x^2 + B\mathbf{J}_y^2 + C\mathbf{J}_z^2 + t_{xxxx}\mathbf{J}_x^4 + t_{xxyy}\mathbf{J}_x^2\mathbf{J}_y^2 + \cdots$$

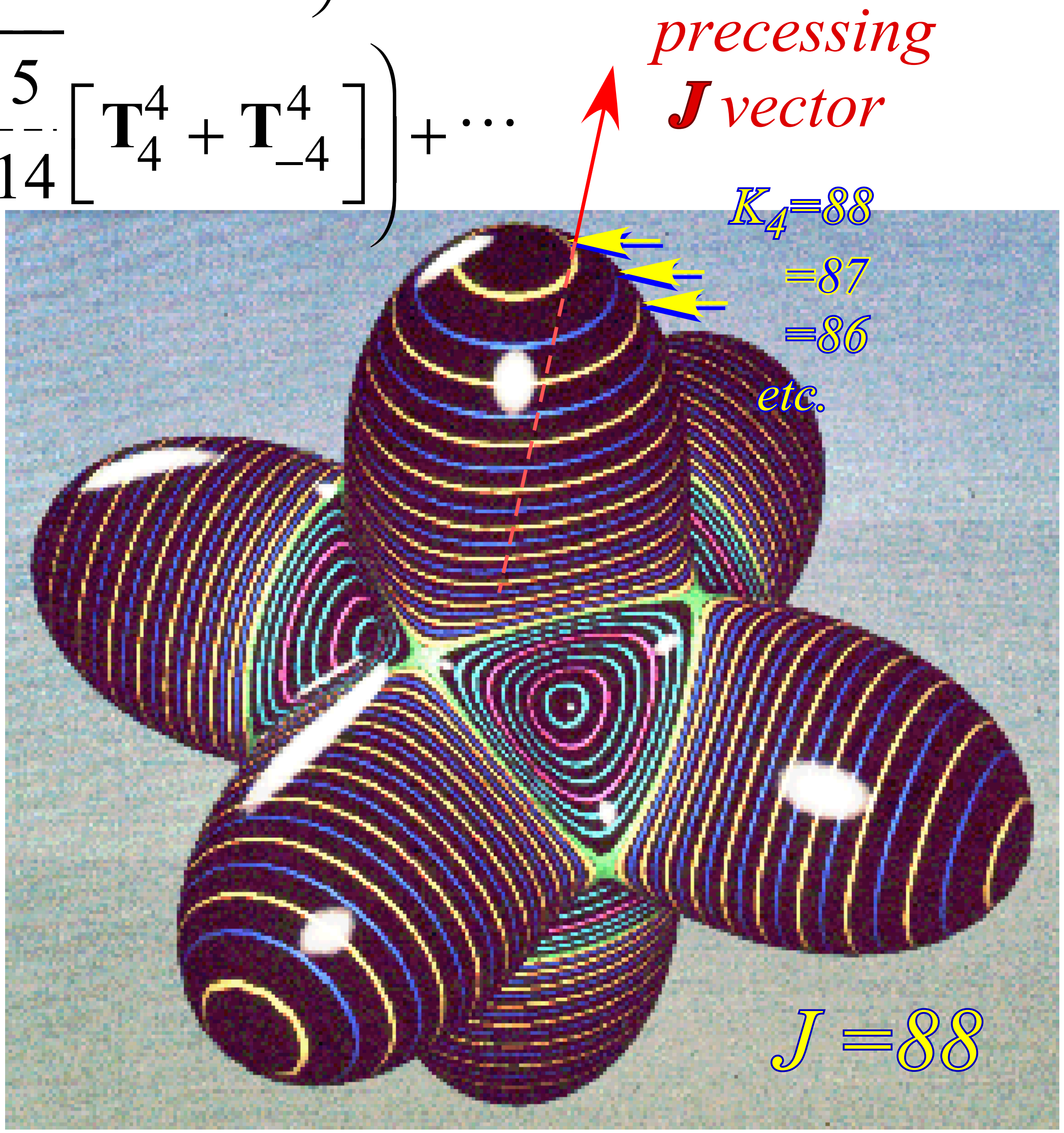
Semi Rigid O_h or T_d Spherical Top: *(Hecht Hamiltonian 1960)*

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

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

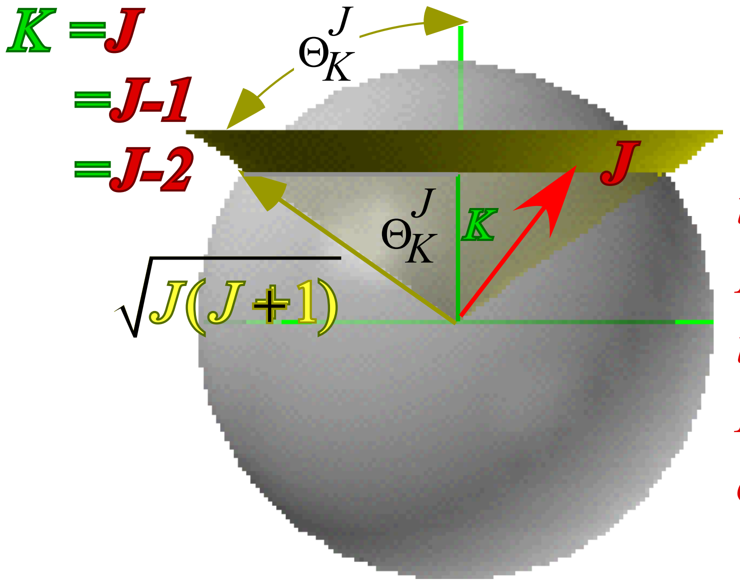


after QTforCA Unit 8. Ch. 25 Fig. 25.4.5



Finding Hamiltonian Eigensolutions by Geometry using Uncertainty Cone Angles

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



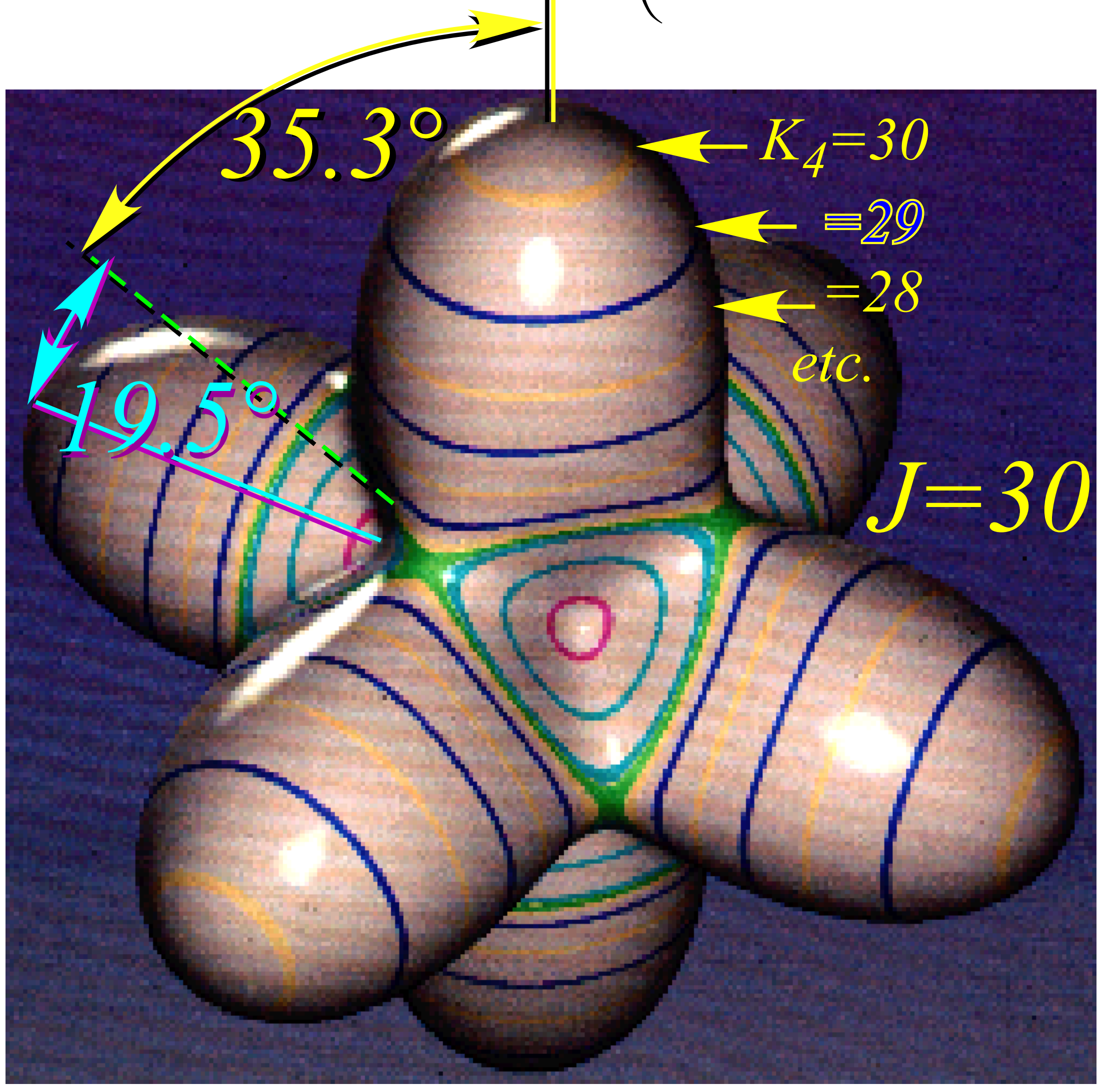
J *cone intersects J=88 RE surface to give approx. K=J, J-1, J-2... energy levels*

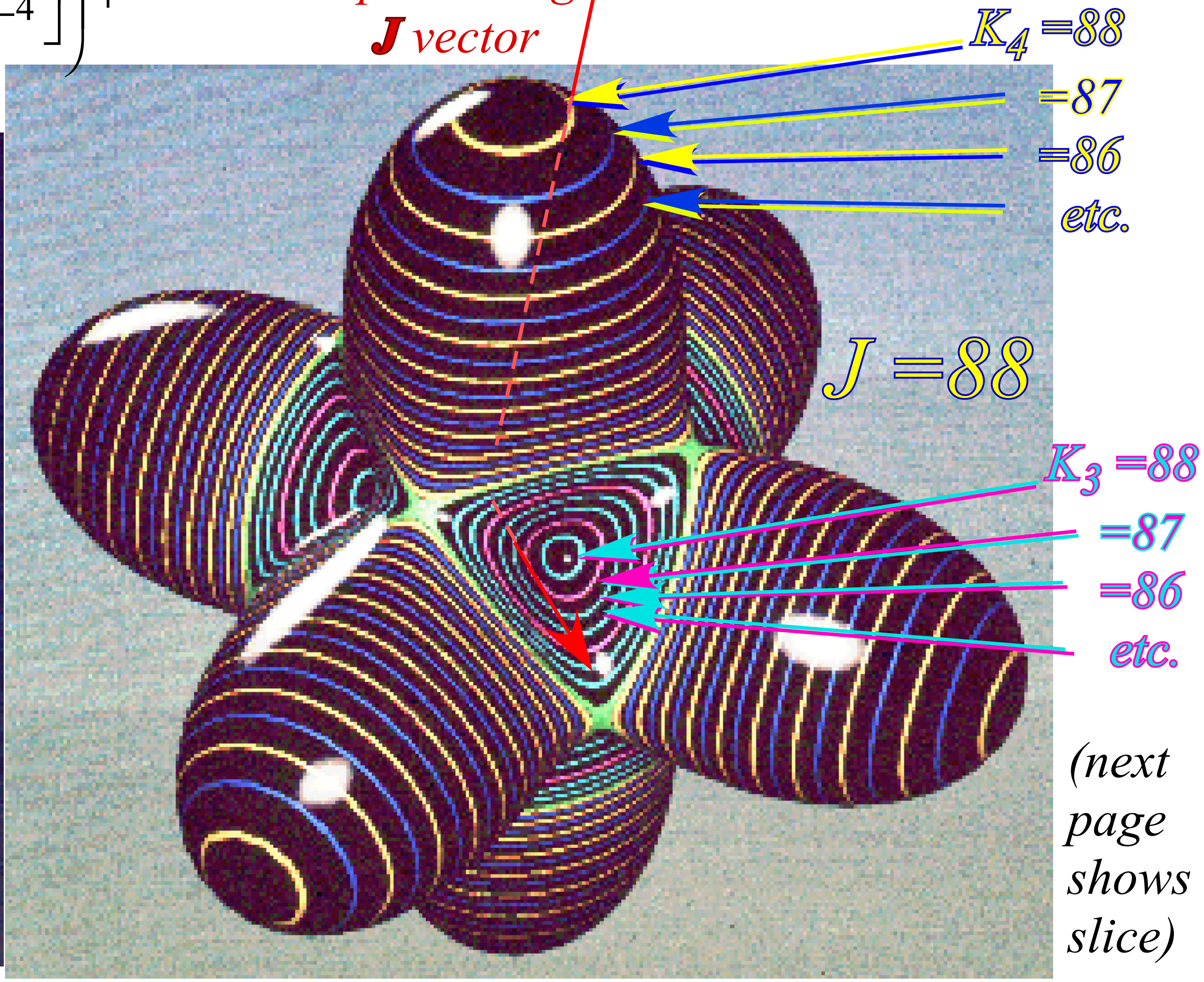
O_h or T_d Spherical Top: *(Hecht Ro-vib Hamiltonian 1960)*

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

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

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





(next page shows slice)

Review: 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

Review: Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

$D_2 \supset C_2$ symmetry correlation

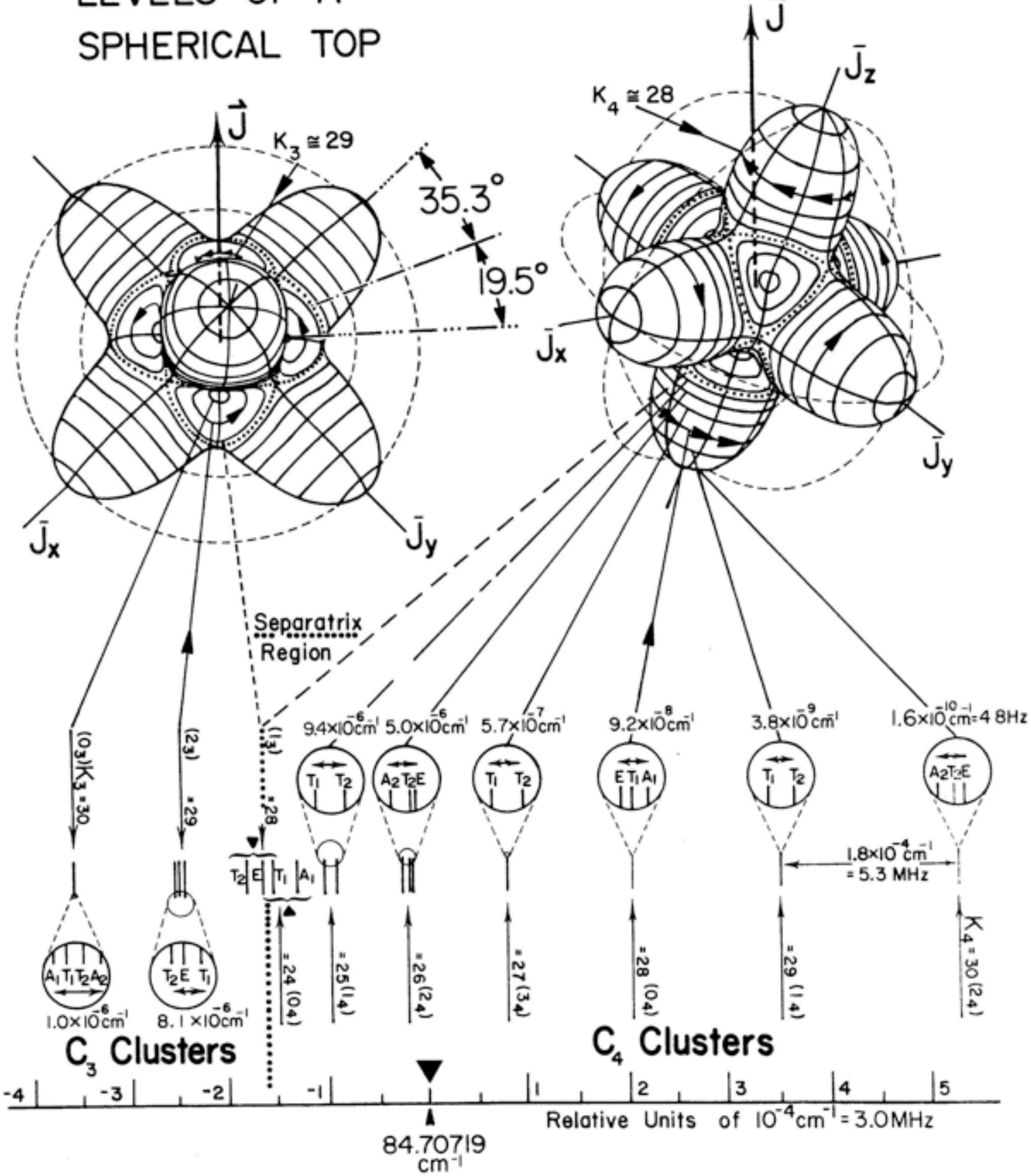
Spherical rotor levels and RES plots

➡ Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...

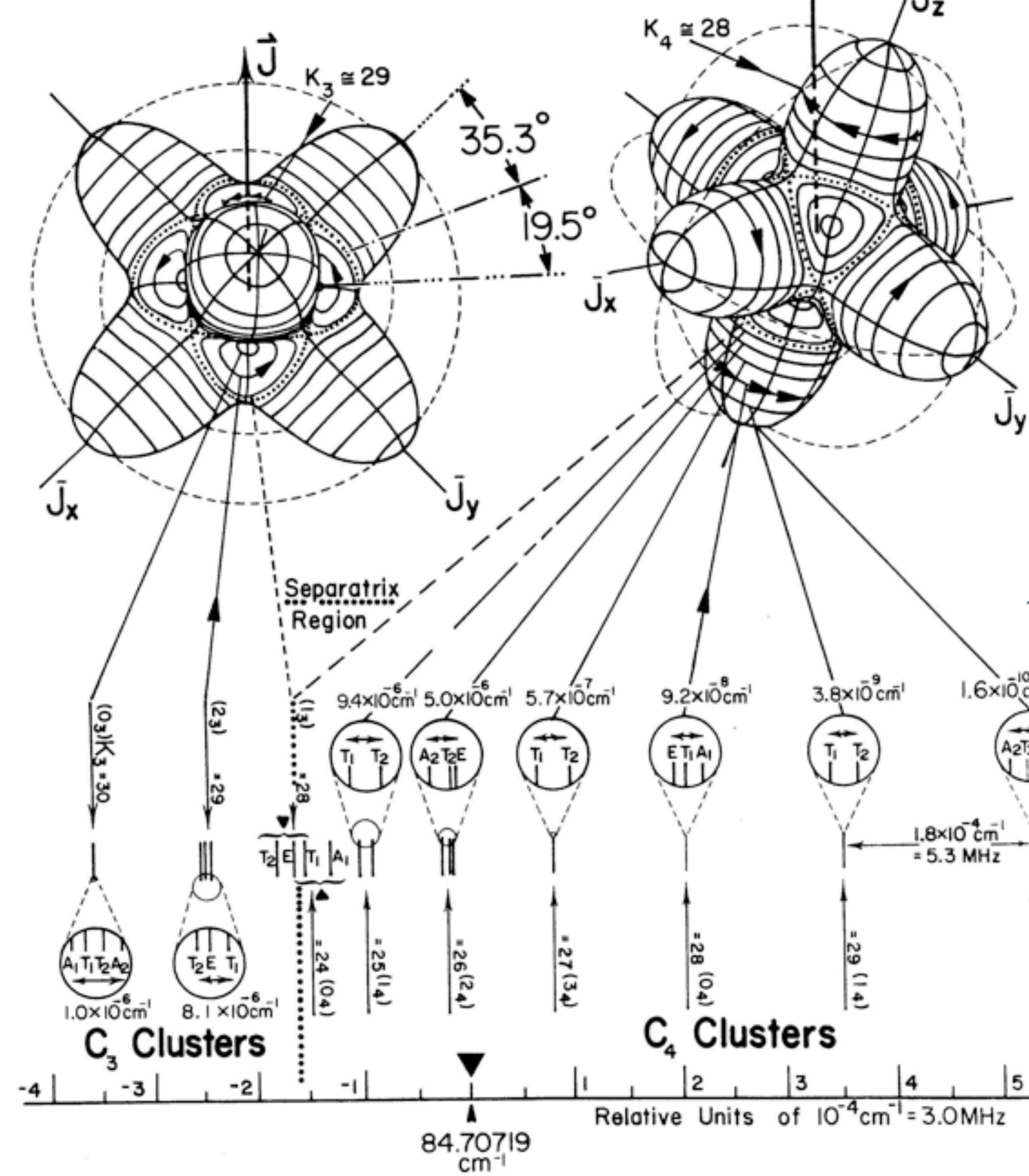
$O \supset C_4$ and $O \supset C_3$ symmetry correlation

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

VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP

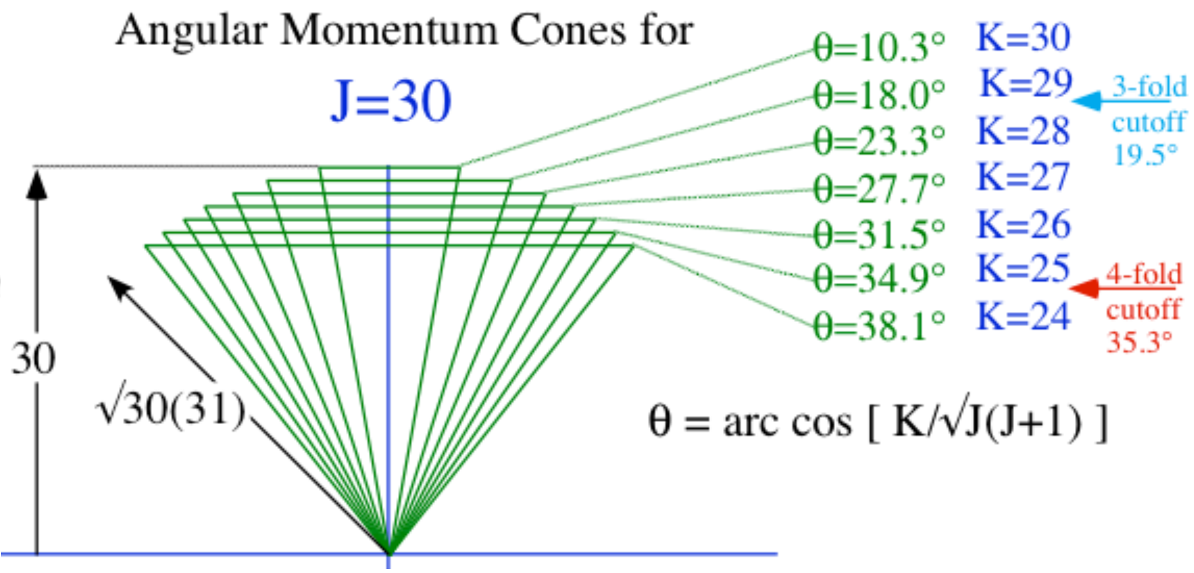


VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP



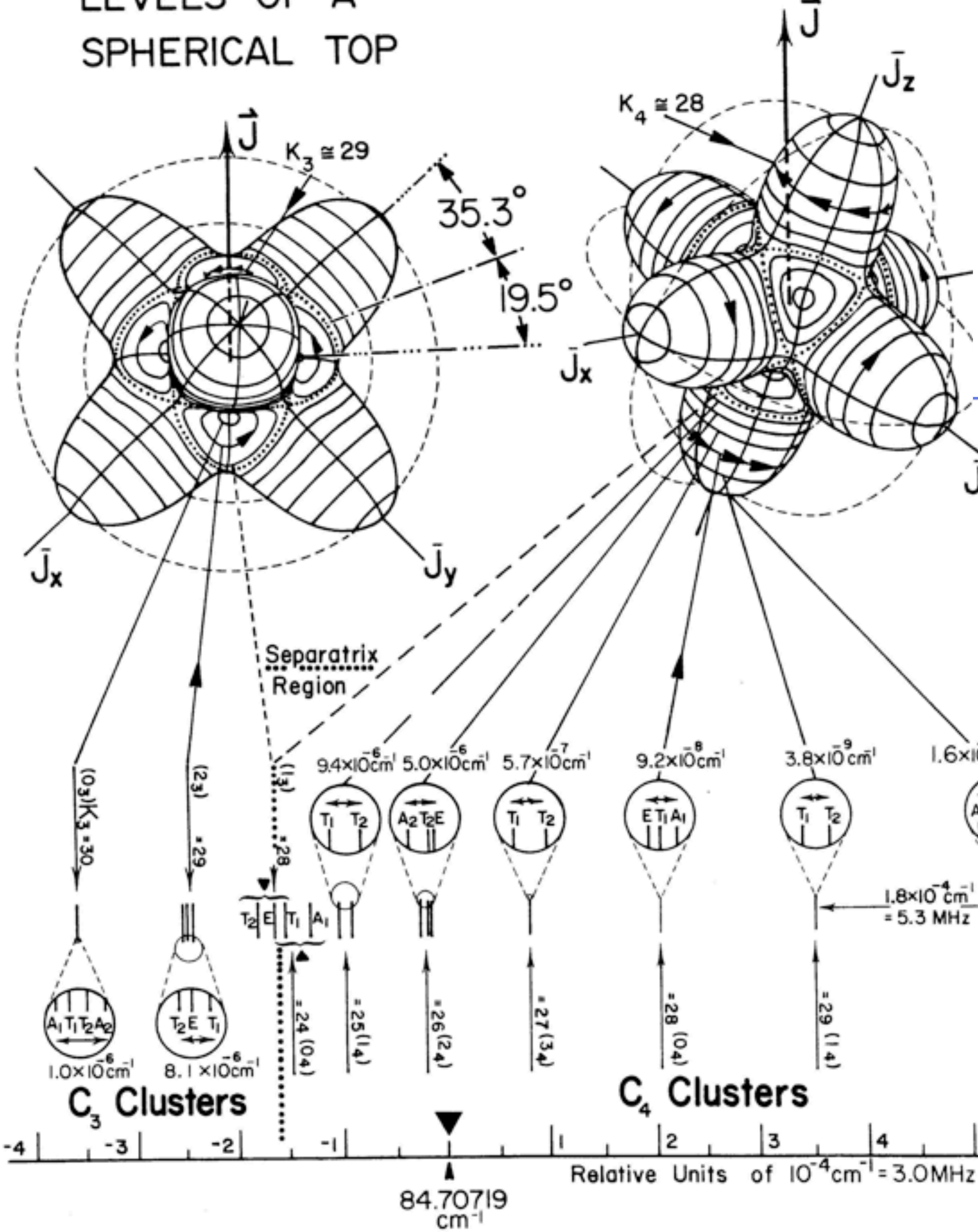
Angular Momentum Cones for

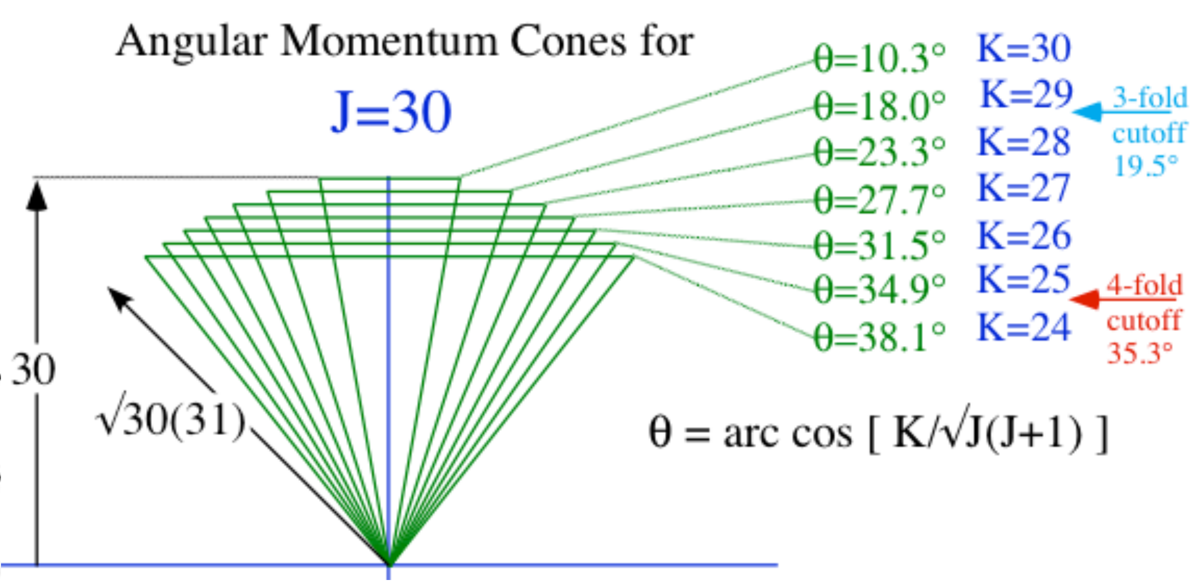
J=30



$$\theta = \text{arc cos}\ [\ K/\sqrt{J(J+1)}\ ]$$

VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP





Angular Momentum Cones for

J=30

θ=10.3° K=30

θ=18.0° K=29 ← 3-fold cutoff 19.5°

θ=23.3° K=28

θ=27.7° K=27

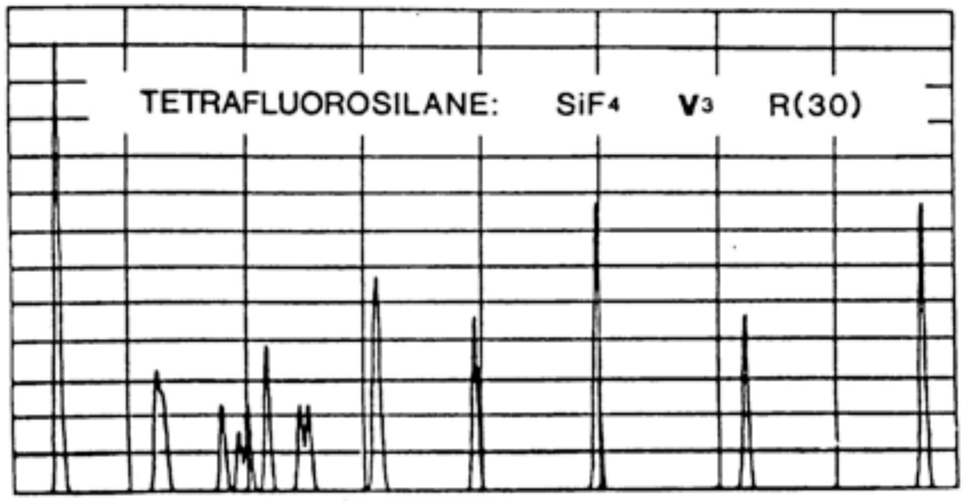
θ=31.5° K=26

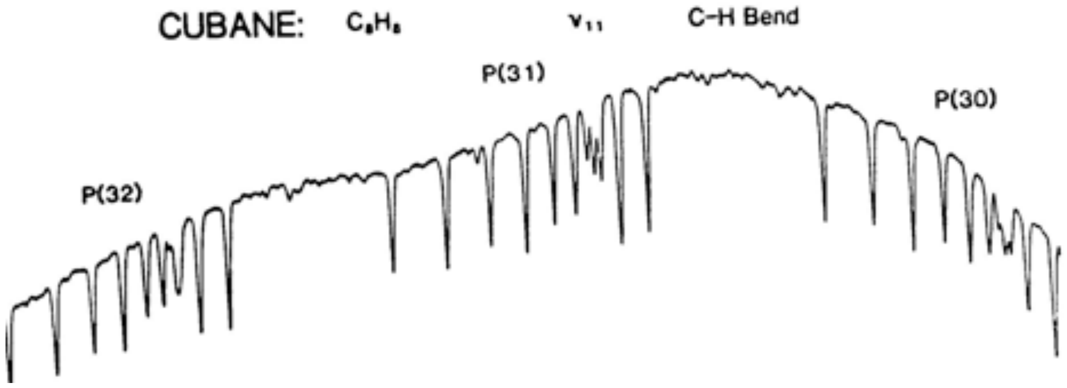
θ=34.9° K=25 ← 4-fold cutoff 35.3°

θ=38.1° K=24

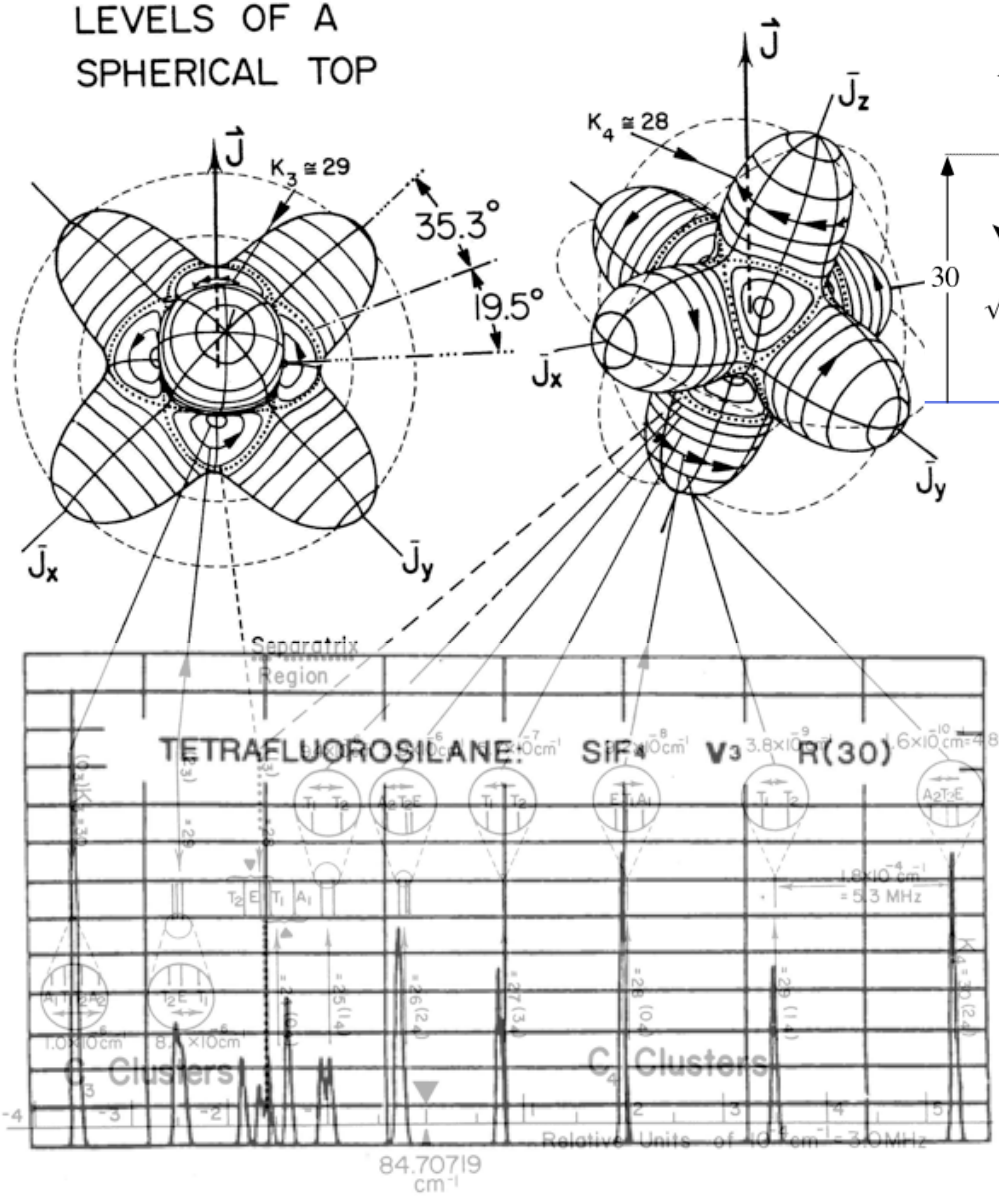
$$\theta = \arccos\left[K/\sqrt{J(J+1)} \right]$$

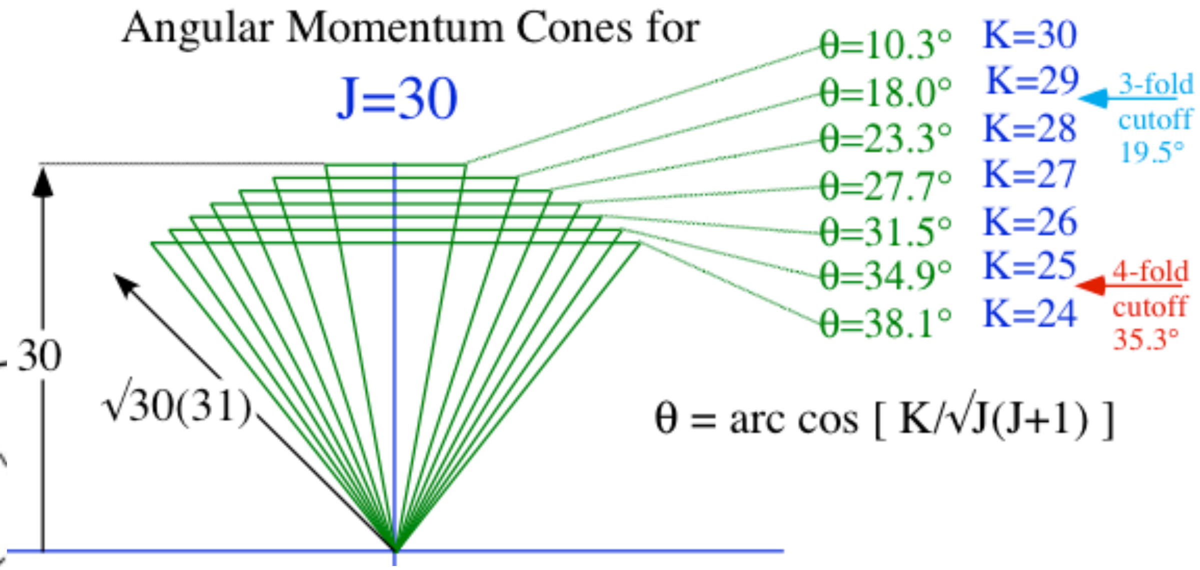
Two molecular examples: SiF_4 and C_8H_8





VISUALIZING THE J = 30 LEVELS OF A SPHERICAL TOP





Angular Momentum Cones for

J=30

θ=10.3° K=30

θ=18.0° K=29 ← 3-fold cutoff 19.5°

θ=23.3° K=28

θ=27.7° K=27

θ=31.5° K=26

θ=34.9° K=25 ← 4-fold cutoff 35.3°

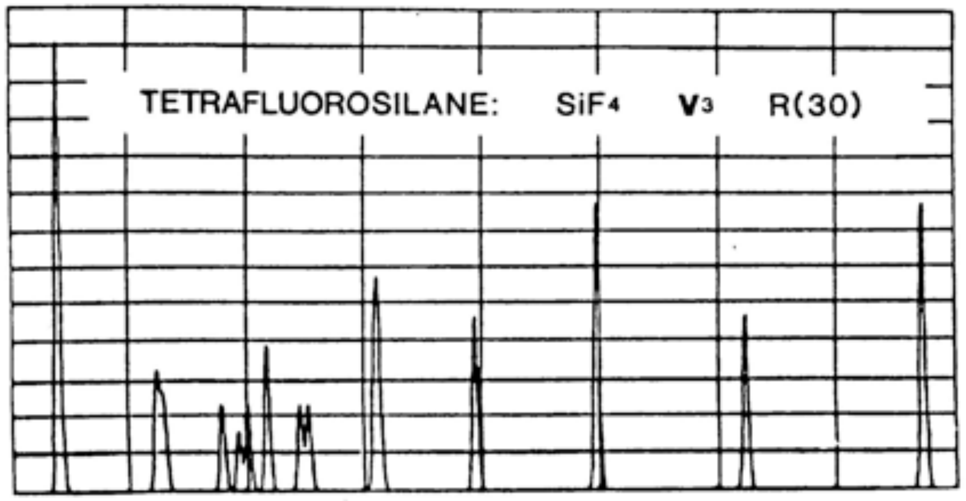
θ=38.1° K=24

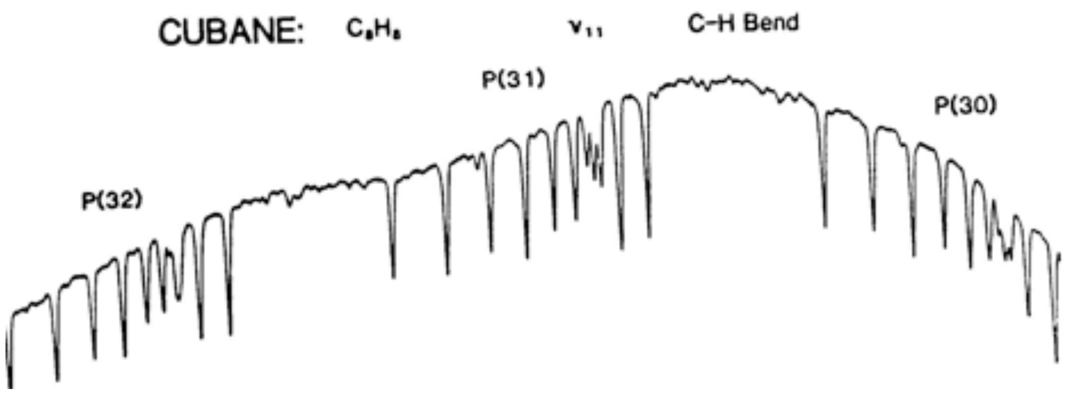
30

√30(31)

θ = arc cos [K/√J(J+1)]

Two molecular examples: SiF₄ and C₈H₈





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 v_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 v_{11} P(30), P(31), and P(32), transitions; cubane (C_8H_8) spectrum from v_{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).]*

Review: 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*

Review: Symmetric rotor levels and RES plots

Asymmetric rotor levels and RES plots

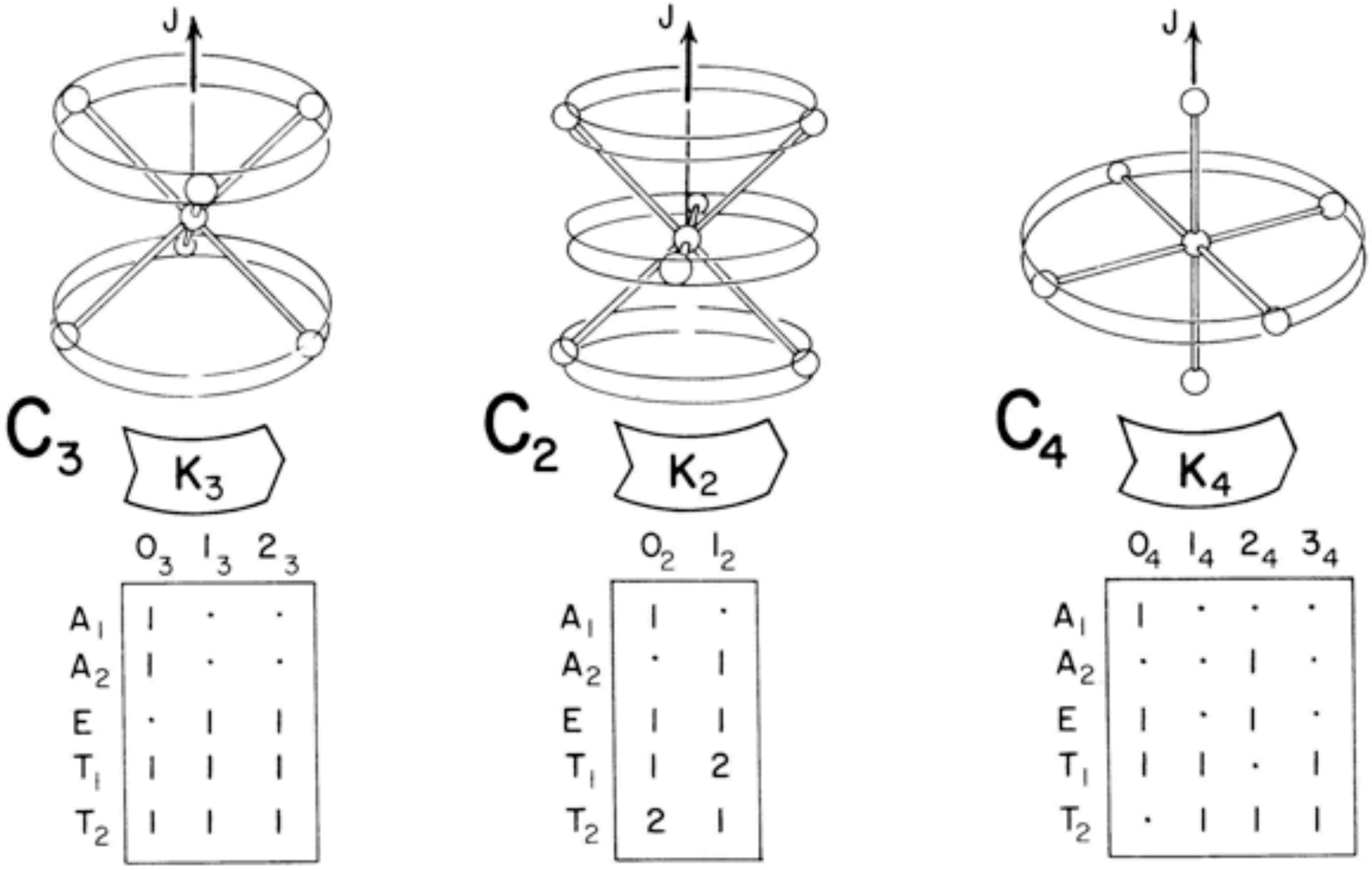
$D_2 \supset C_2$ *symmetry correlation*

Spherical rotor levels and RES plots

Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...

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

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



	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

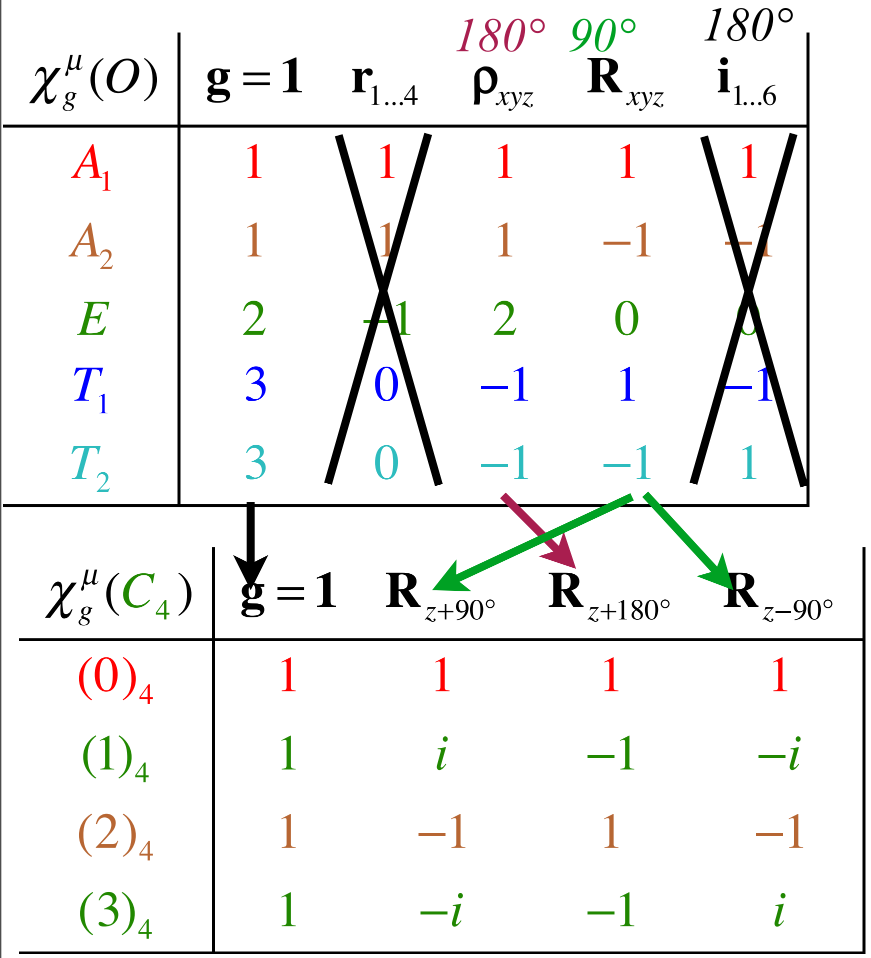
	0_2	1_2
A_1	1	·
A_2	·	1
E	1	1
T_1	1	2
T_2	2	1

	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

Octahedral $O\supset C_4$ subgroup correlations



$\chi^{\mu}_{g}(O)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1\ldots4}$	180° $\boldsymbol{\rho}_{xyz}$	90° $\mathbf{R}_{xyz}$	180° $\mathbf{i}_{1\ldots6}$
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

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

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

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

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

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

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

$O\downarrow C_4$ 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 $O \supset C_4$ subgroup correlations

			180°	90°	180°
$\chi_g^\mu(O)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1...4}$	$\boldsymbol{\rho}_{xyz}$	$\mathbf{R}_{xyz}$	$\mathbf{i}_{1...6}$
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~~

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

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

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

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

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

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

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

$O\downarrow C_4$ 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

$\chi_g^\mu(O)$	$\mathbf{g}=\mathbf{1}$	$\mathbf{r}_{1...4}$	$\boldsymbol{\rho}_{xyz}$	$\mathbf{R}_{xyz}$	$\mathbf{i}_{1...6}$
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	$e^{-i2\pi/3}$	$e^{i2\pi/3}$

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

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

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

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

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

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

$O\downarrow C_3$ subduction

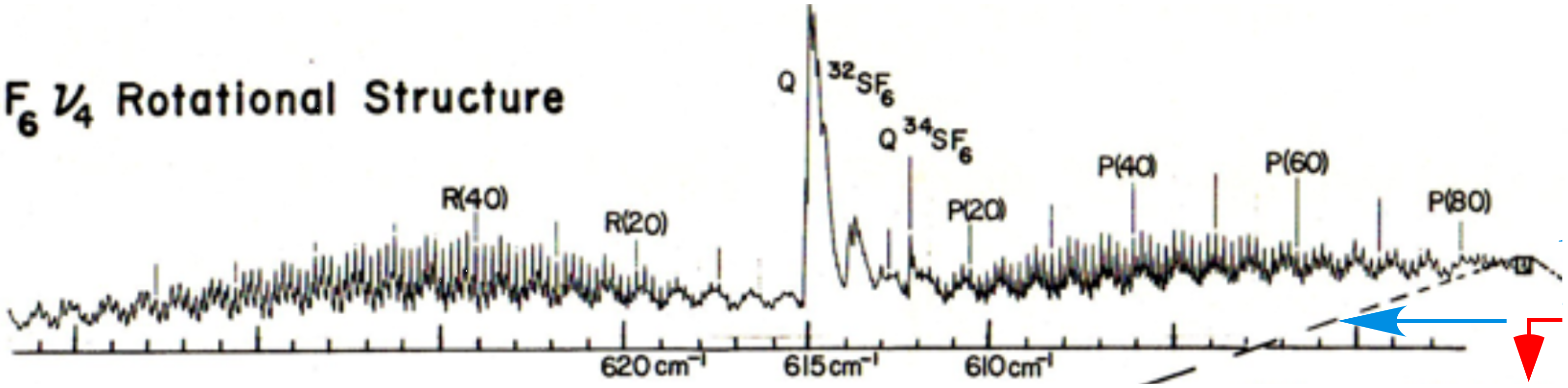
$O\downarrow C_4$	0_3	1_3	$2_3=\bar{1}_3$
A_1	1	·	·
A_2	1	·	·
E	·	1	1
T_1	1	1	1
T_2	1	1	1

Review: 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*

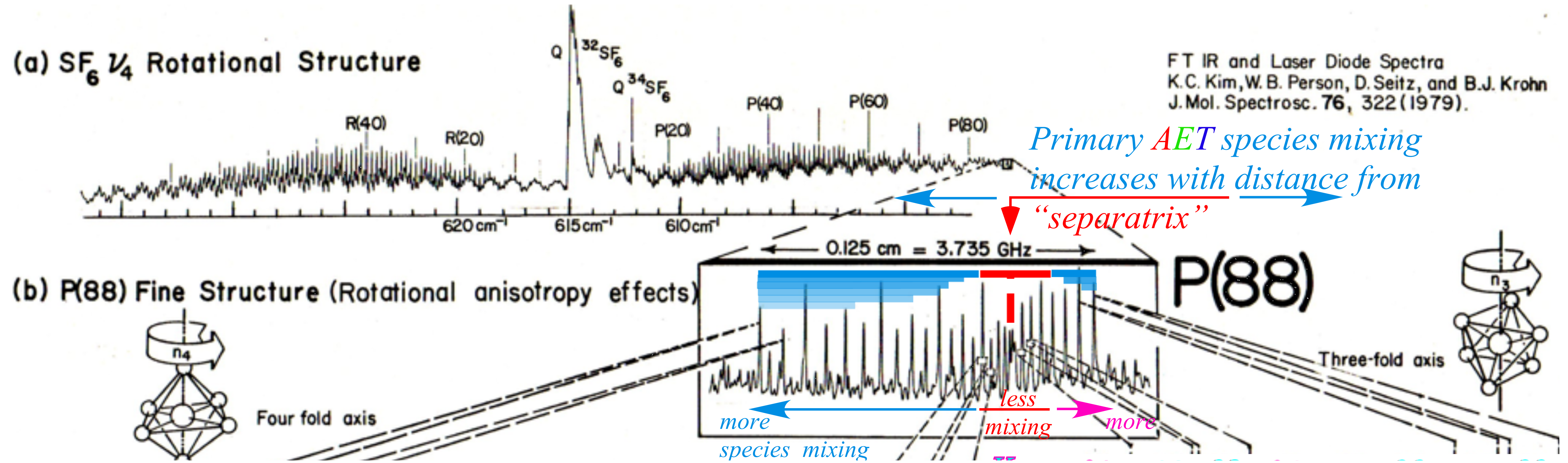
Review: Symmetric rotor levels and RES plots

- *Asymmetric rotor levels and RES plots*
    - $D_2 \supset C_2$ *symmetry correlation*
- *Spherical rotor levels and RES plots*
    - *Spectral fine structure of* SF_6, SiF_4, C_8H_8, CF_4,...
    - $O \supset C_4$ *and* $O \supset C_3$ *symmetry correlation*

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



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

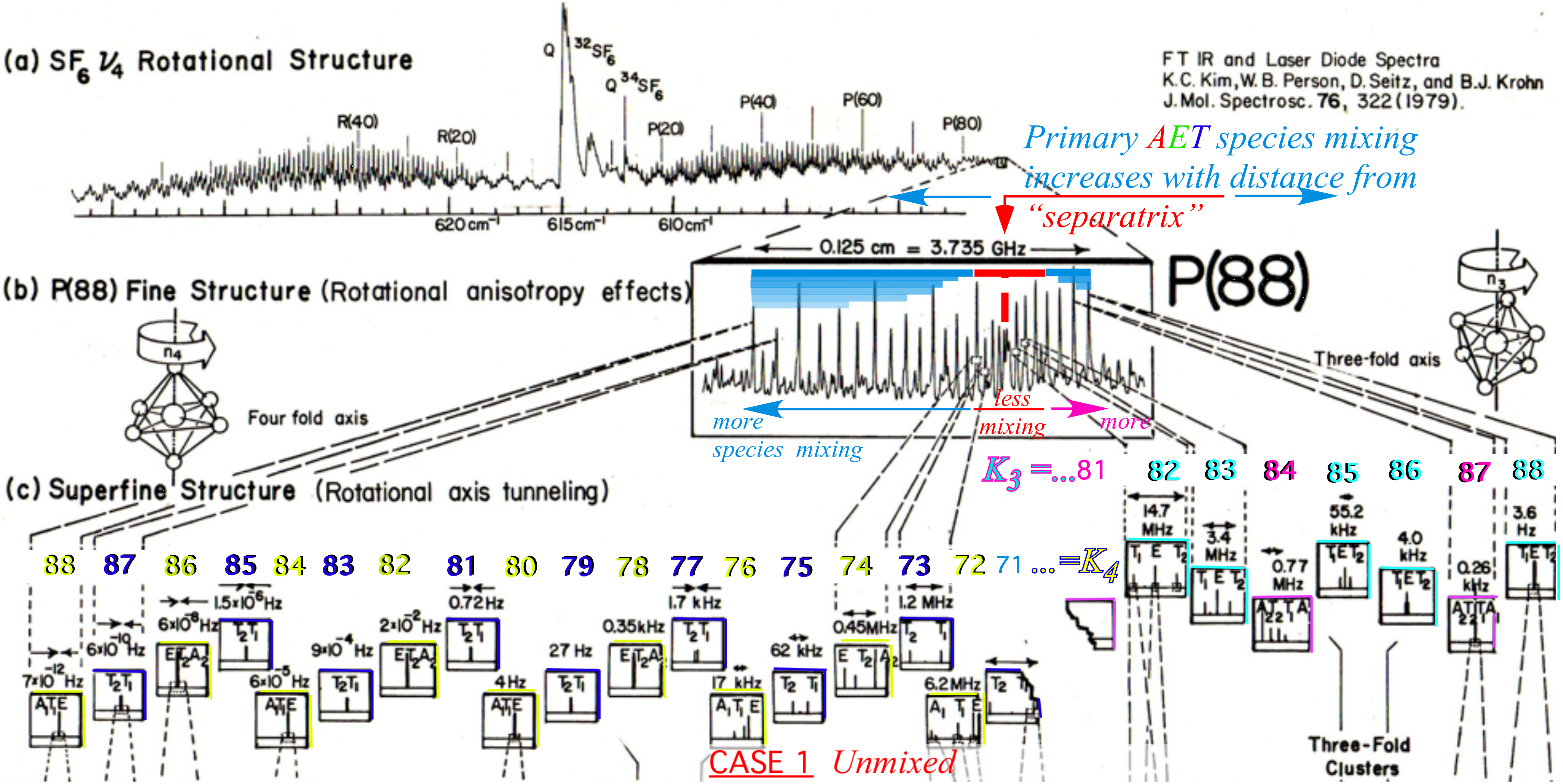


Primary AET species mixing increases with distance from "separatrix"

more species mixing

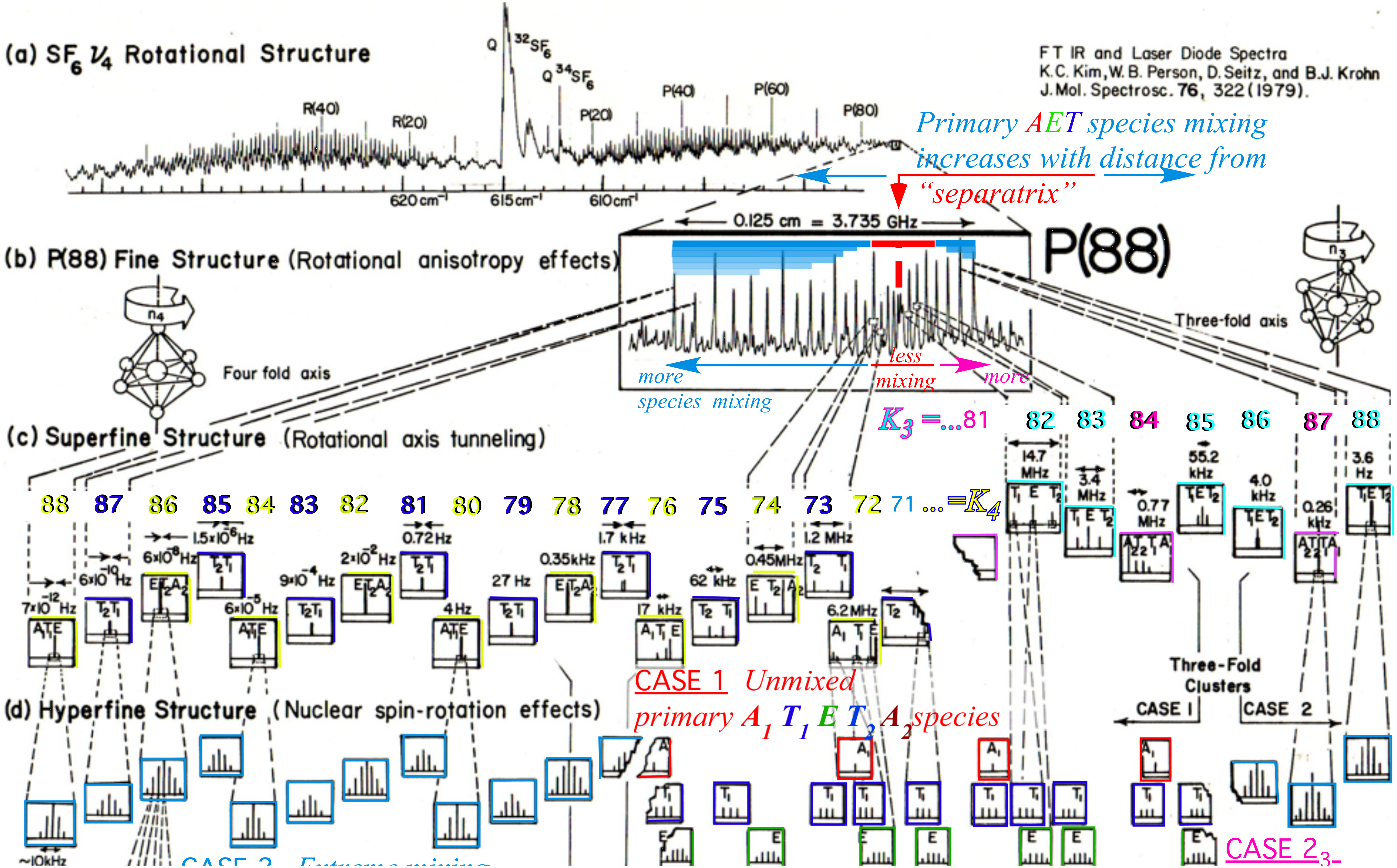
less mixing

more



Primary AET species mixing increases with distance from "separatrix"

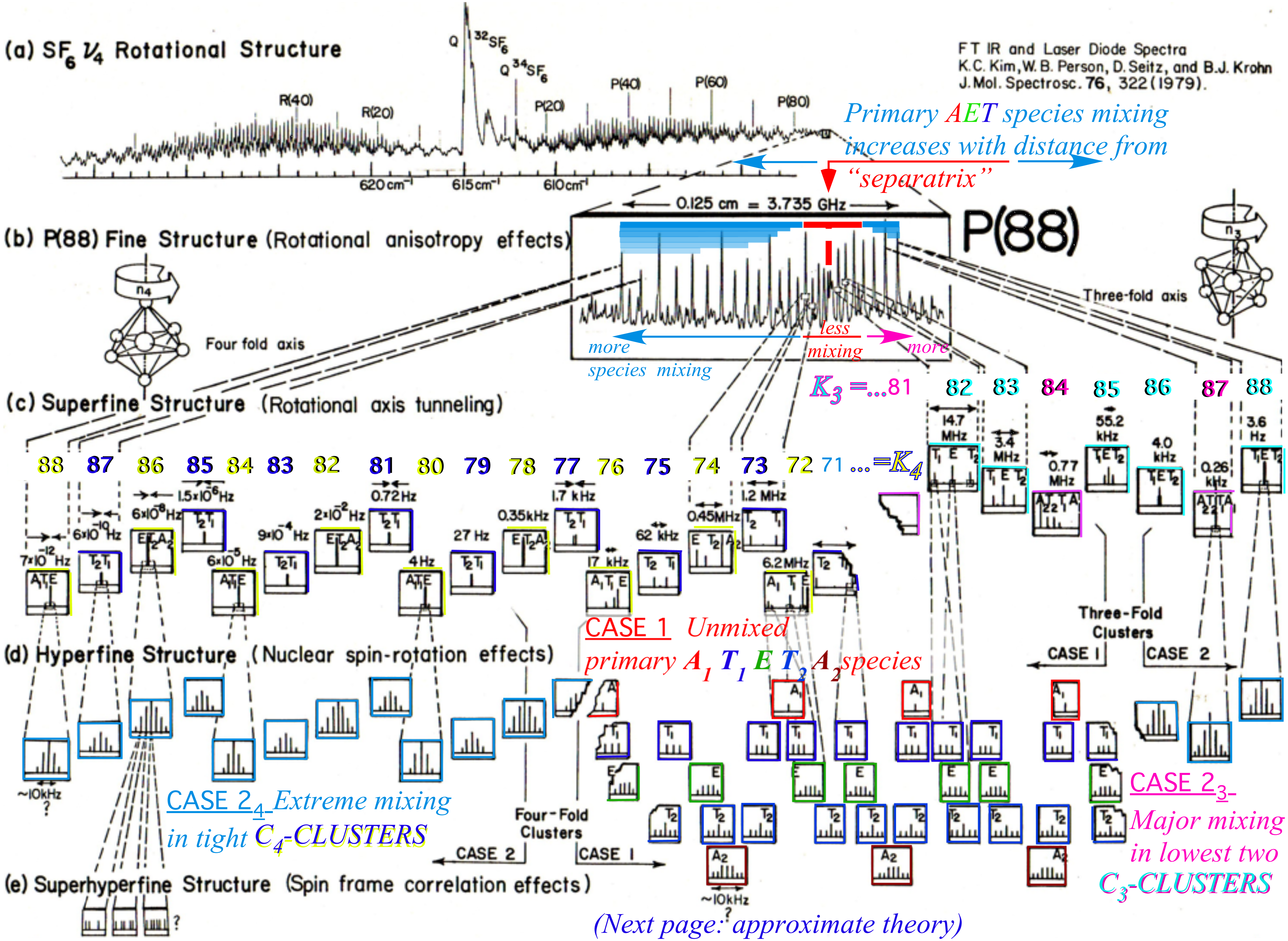
CASE 1 *Unmixed*



Primary AET species mixing increases with distance from "separatrix"

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

CASE 2_3



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"

more species mixing

less mixing

more

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

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

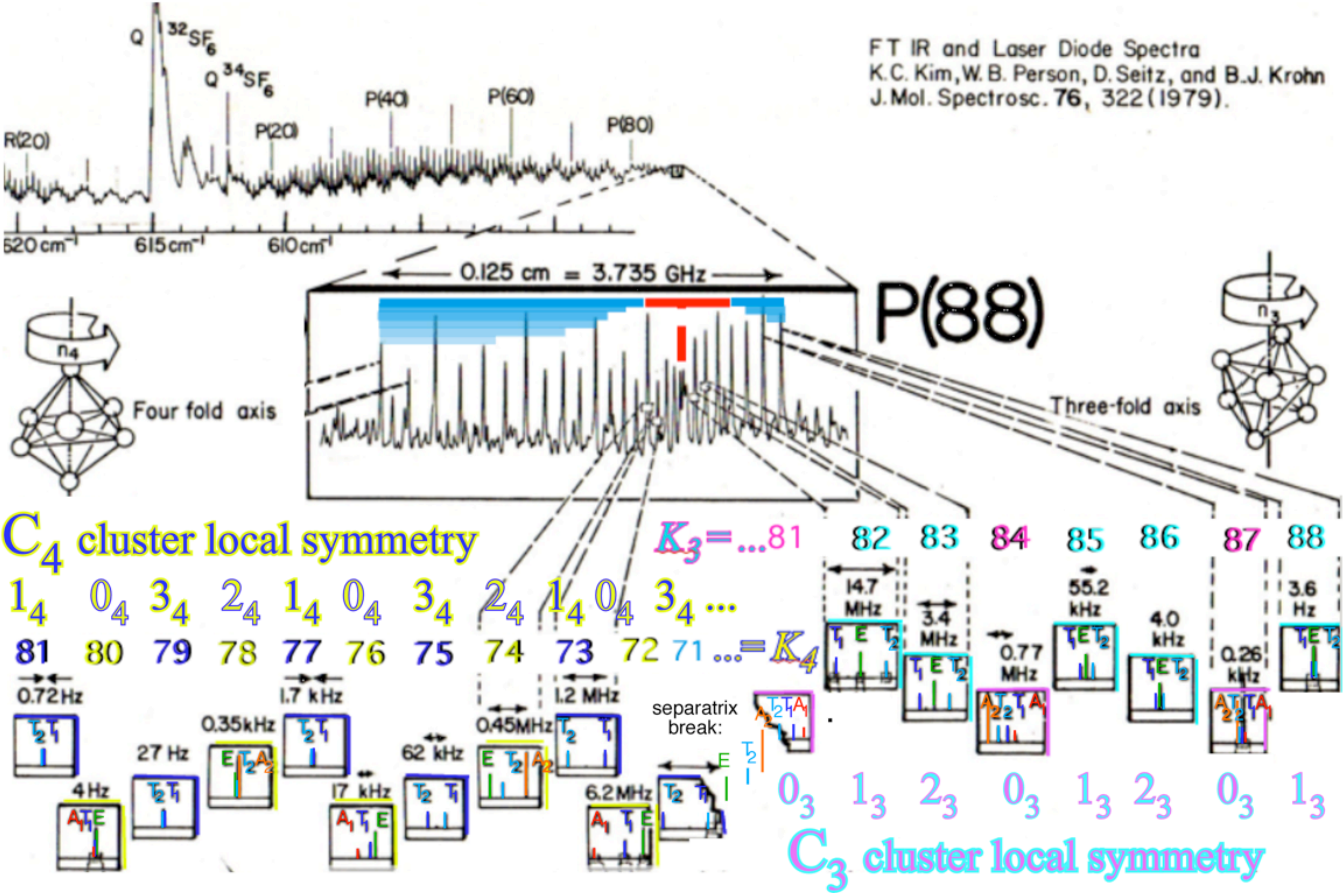
CASE 1 *Unmixed primary A_1 T_1 E T_2 A_2 species*

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

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

(Next page: approximate theory)

IR Spectra of SF6 ν₄ P(88)



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

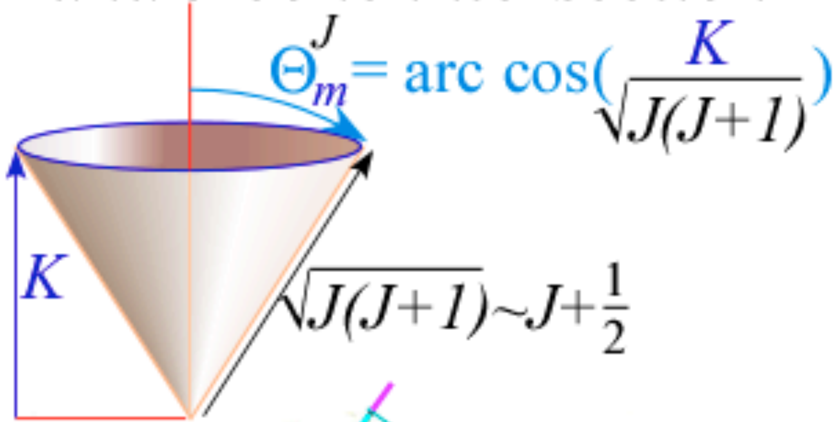
Int.J.Molecular Science 14.(2013) Fig.26 p. 783

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

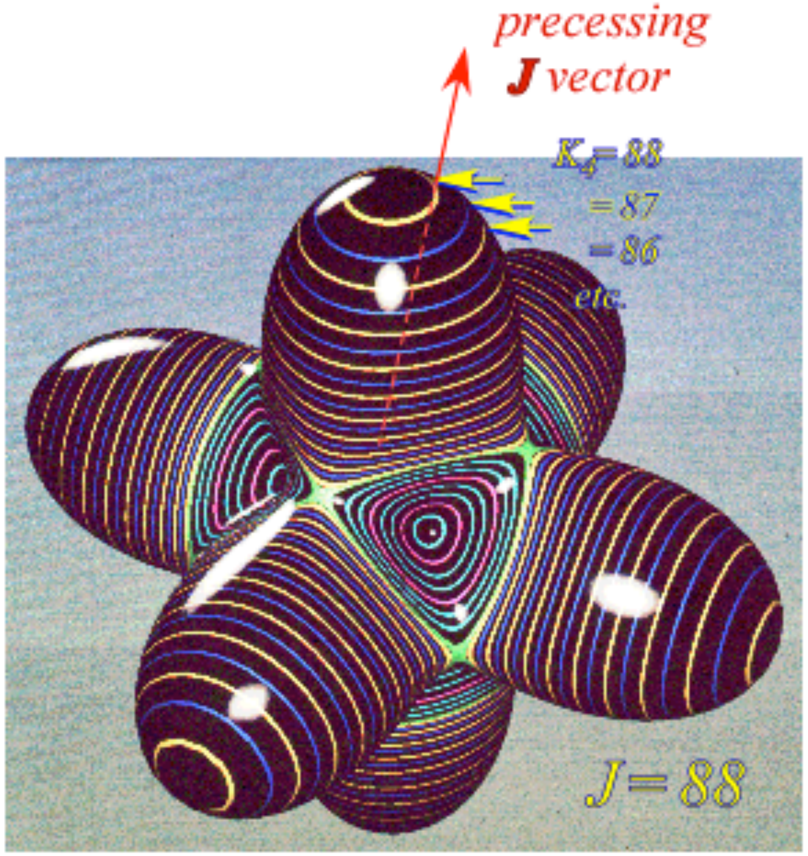
$$\mathbf{H} = B\left(\mathbf{J}_x^2+\mathbf{J}_y^2+\mathbf{J}_z^2\right)+t_{440}\left(\mathbf{J}_x^4+\mathbf{J}_y^4+\mathbf{J}_z^4-\frac{3}{5}J^4\right)+\cdots$$

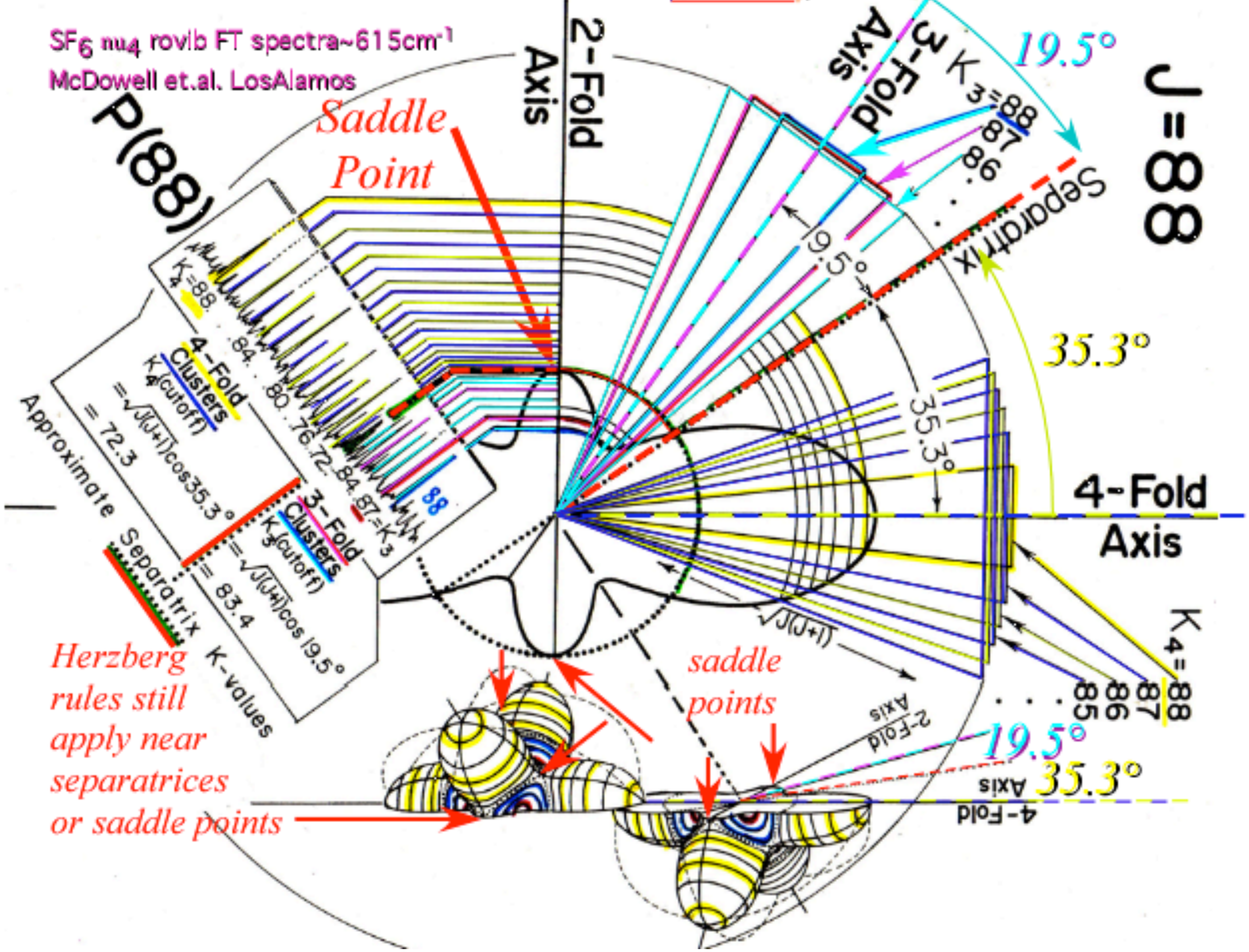
$$= \quad B\mathbf{J}^2 \quad +t_{440}\left(\mathbf{T}_0^4+\sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4+\mathbf{T}_{-4}^4\right]\right)+\cdots$$

and J-cone intersection



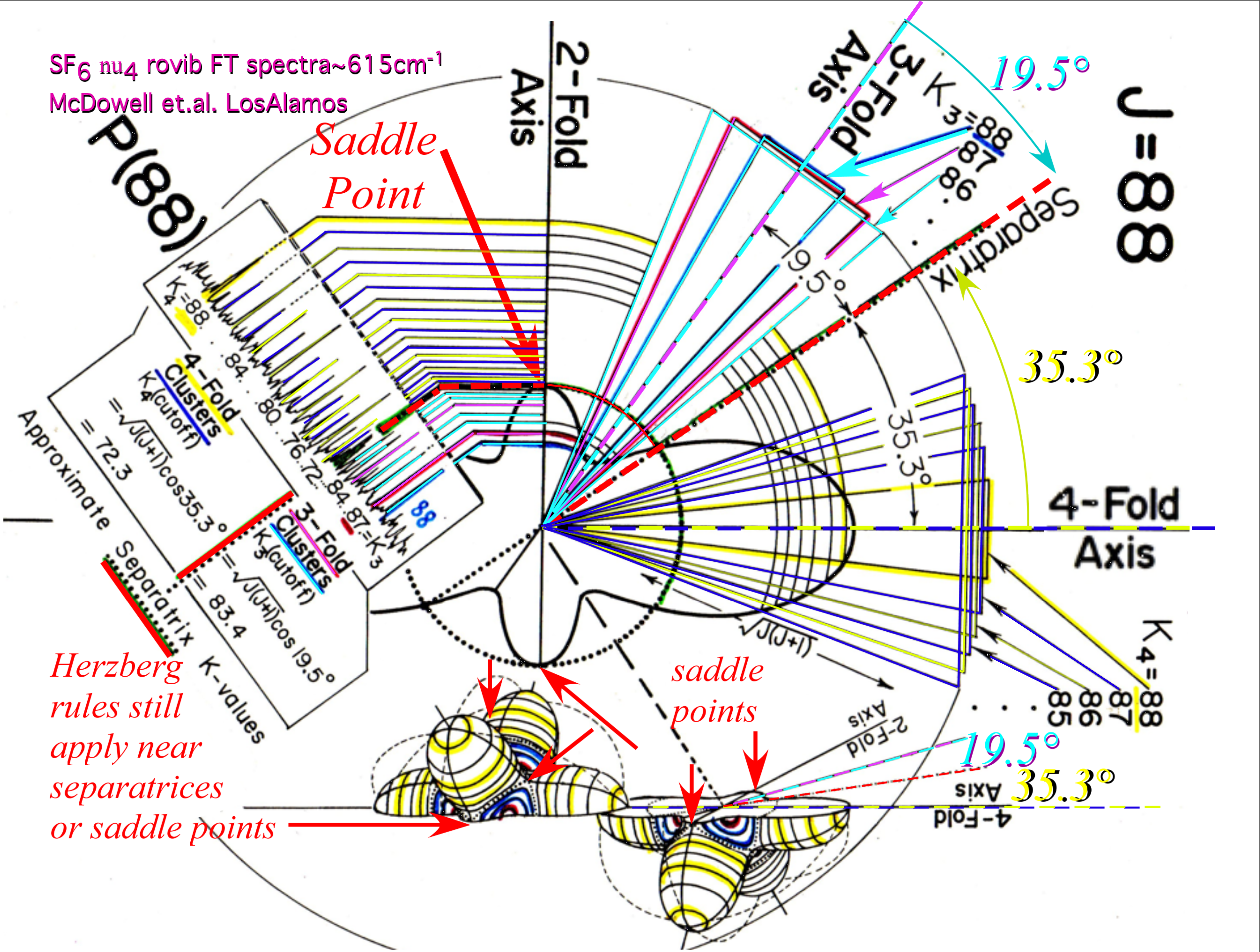
Rovibronic Energy (RE) Tensor Surface





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

McDowell et.al. LosAlamos



Saddle Point

Herzberg rules still apply near separatrices or saddle points

saddle points

Review: 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*
Review: Symmetric rotor levels and RES plots
Asymmetric rotor levels and RES plots
$D_2 \supset C_2$ *symmetry correlation*
Spherical rotor levels and RES plots
Spectral fine structure of SF_6, SiF_4, C_8H_8, CF_4,...
$O \supset C_4$ *and* $O \supset C_3$ *symmetry correlation*
Details of P(88) v_4 SF_6 *spectral structure and implications*
Beginning theory with graphical approaches
➡ *Rovibronic nomograms and PQR structure*
Rovibronic energy surfaces (RES) and cone geometry
Spin symmetry correlation, tunneling, and entanglement
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

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

to help understand complex rotational spectra and dynamics.

OUTLINE

	Example(s)
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
	$\nu_3/2\nu_4$

Graphical approach to rotation-vibration-spin Hamiltonian

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

OUTLINE

Introductory review

	Example(s)
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and Θ^{ℓ}_{K}-cones*	ν_4 P(88) SF_6
• *Spin symmetry correlation tunneling and entanglement*	SF_6

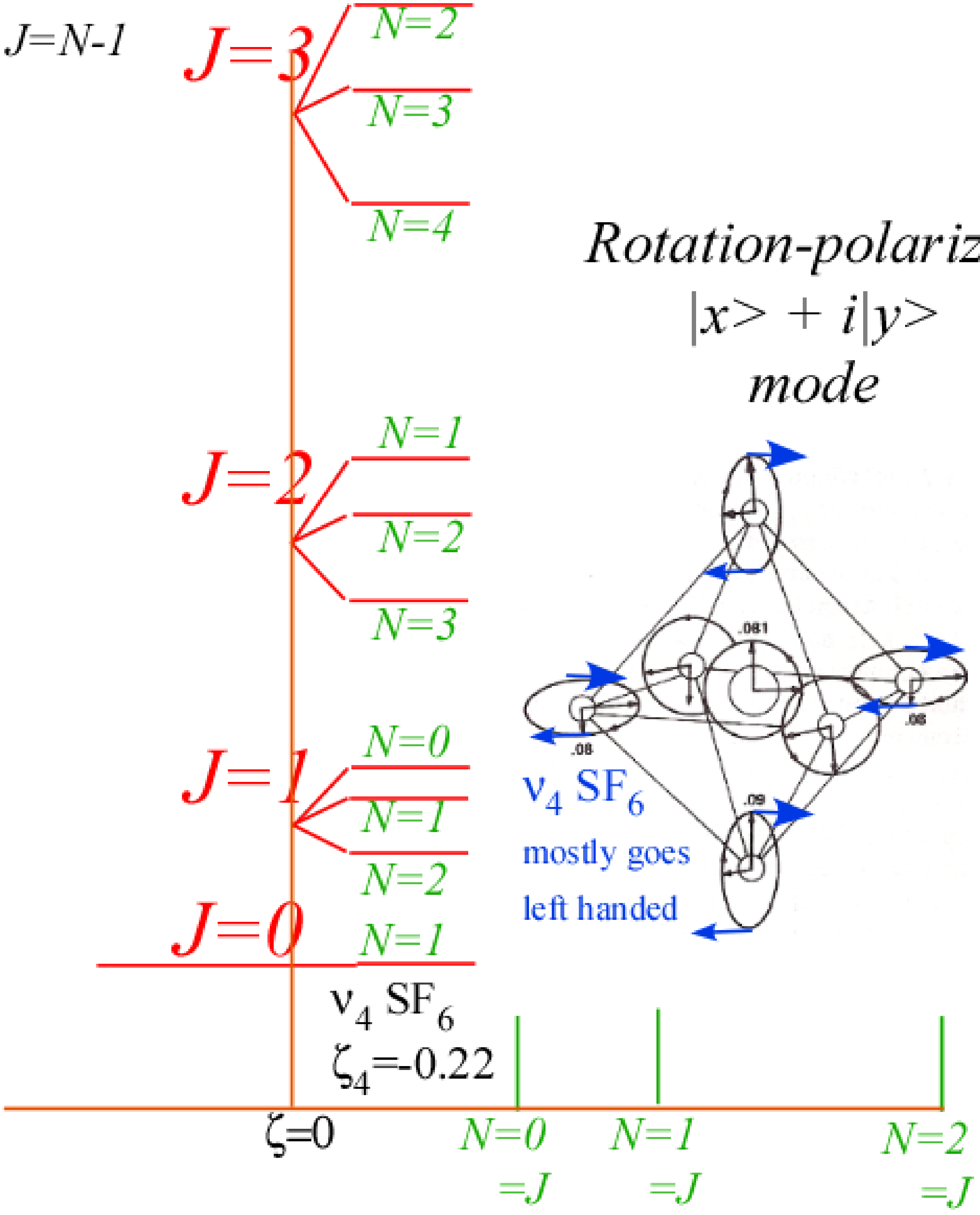
Recent developments

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

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

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

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



Rotation-polarized
$|x\rangle + i|y\rangle$
mode

ν_4 SF$_6$
mostly goes
left handed

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

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

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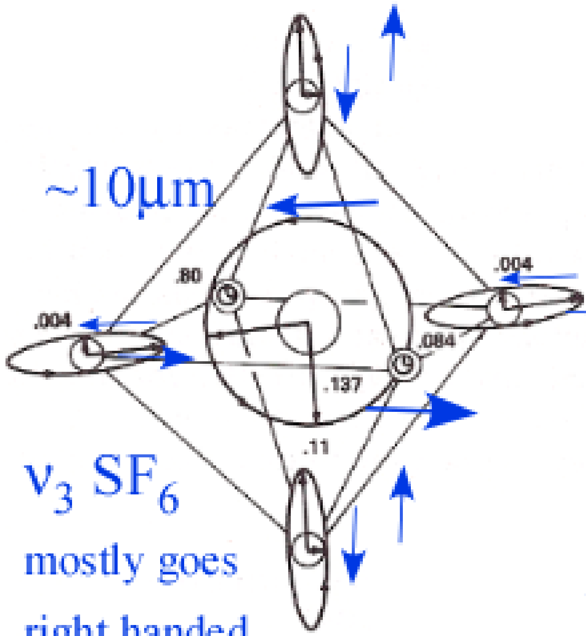
$$= -B\zeta\,[\,J(J+1) - N(N+1) + \ell(\ell+1)]$$

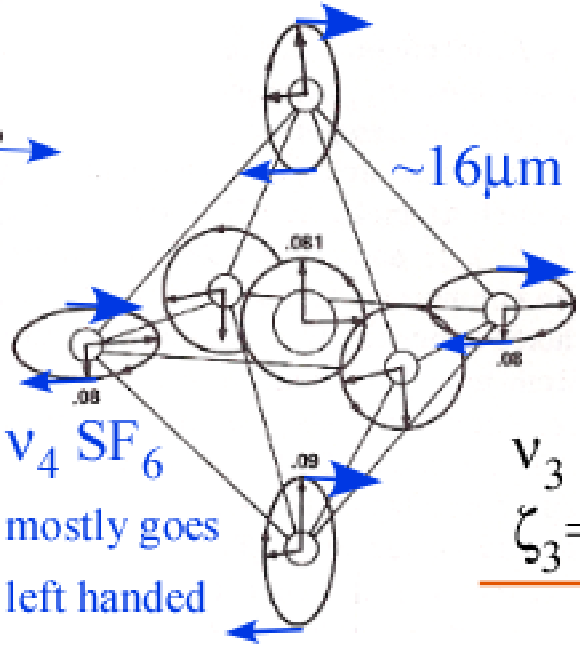


~10μm

ν_3 SF$_6$

mostly goes

right handed

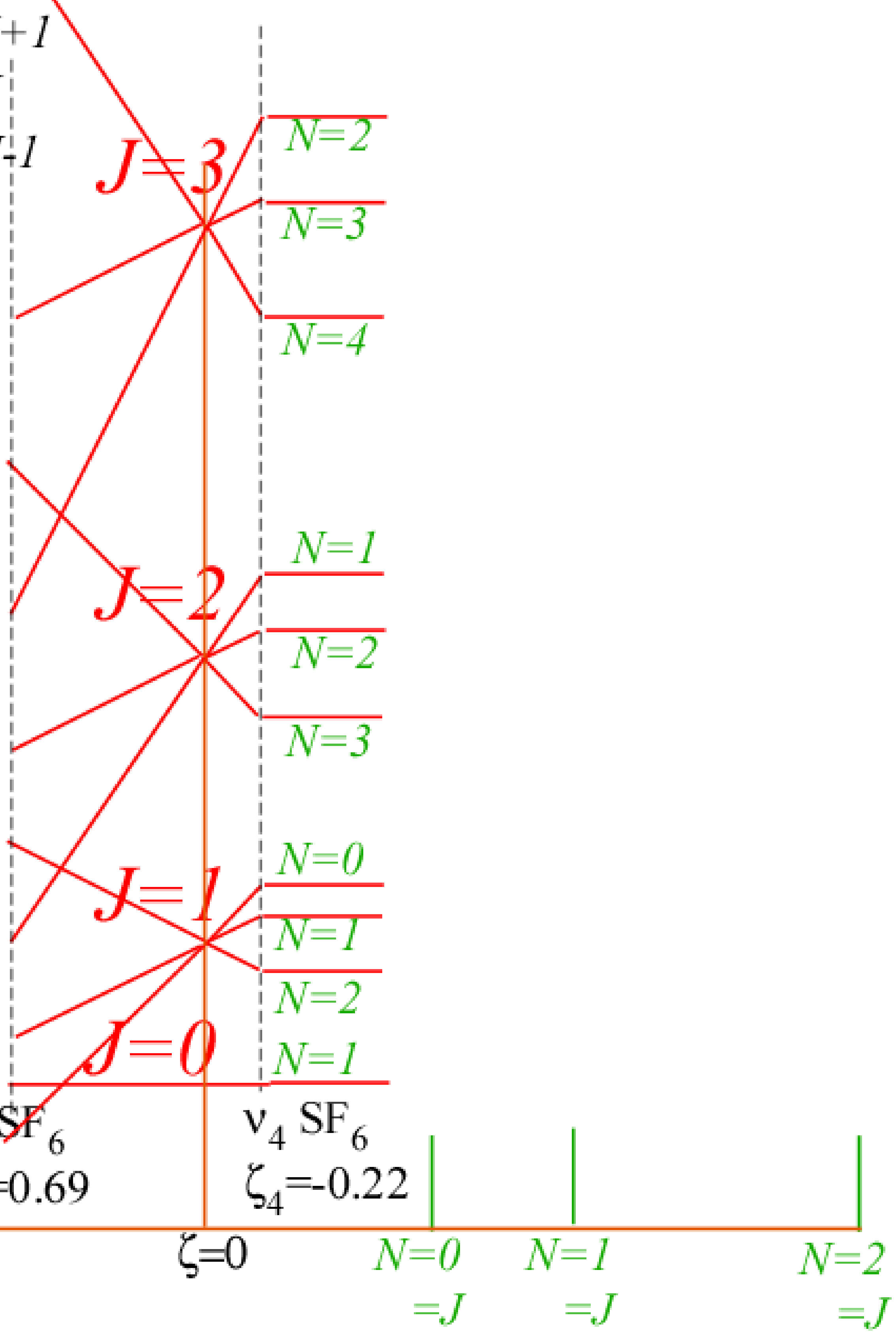


~16μm

ν_4 SF$_6$

mostly goes

left handed



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

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

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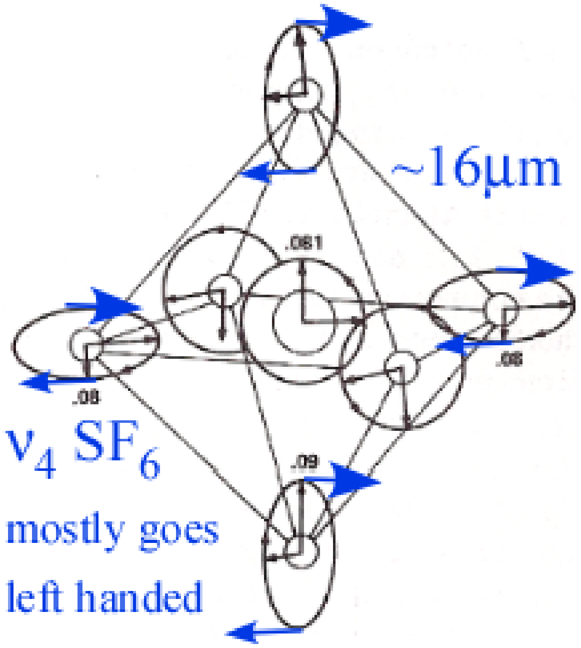
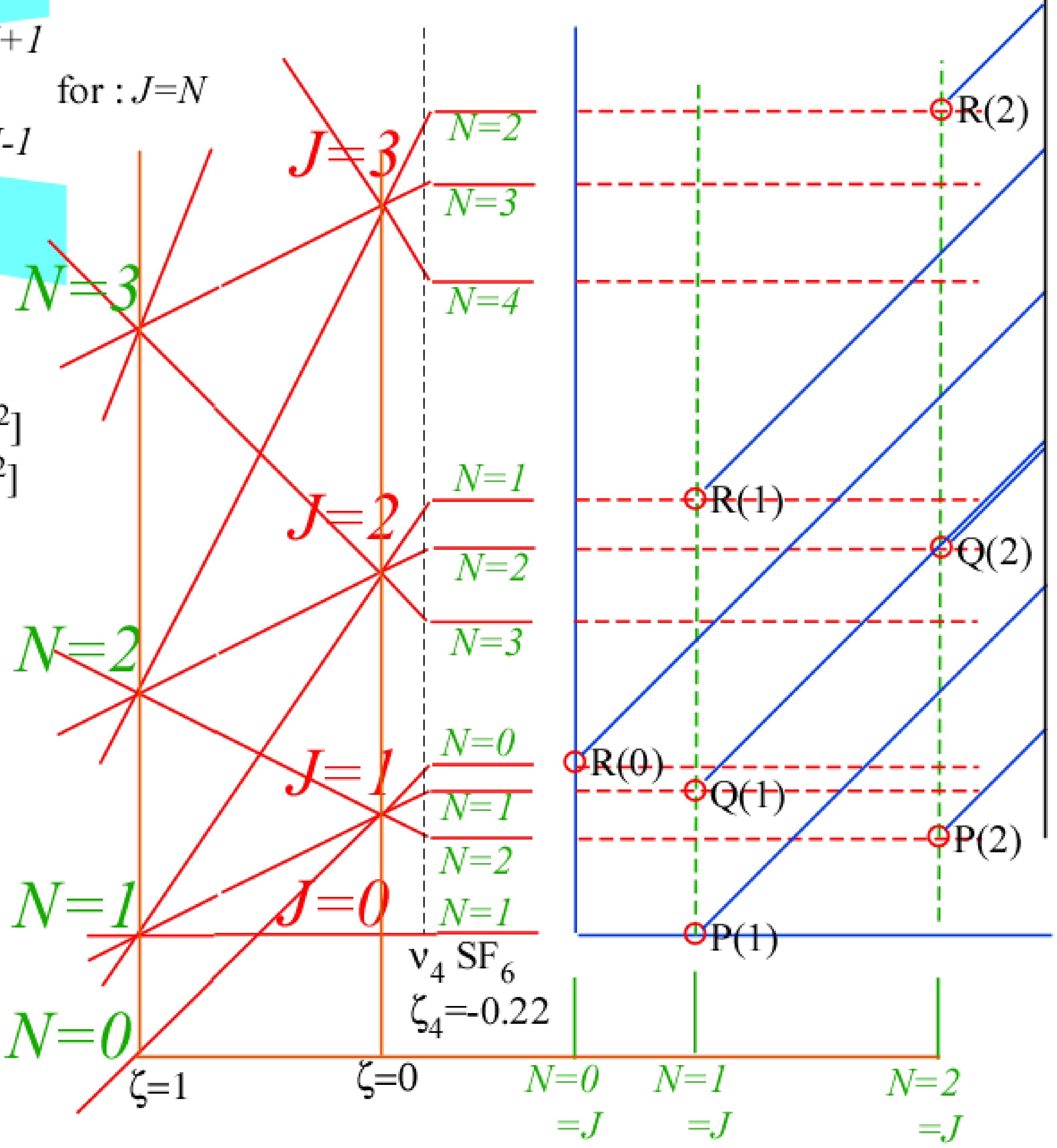
$$= -B\zeta[\ J(J+1)-N(N+1)+\ell(\ell+1)]$$



ν_4 SF_6

mostly goes left handed



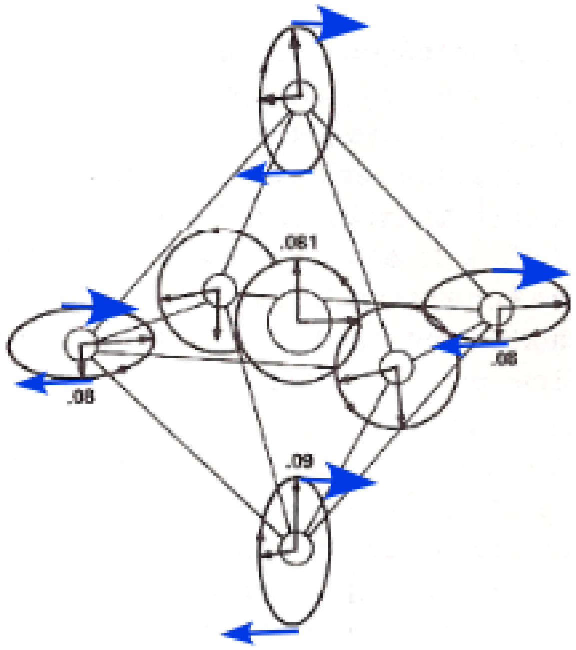
ν_4 SF_6

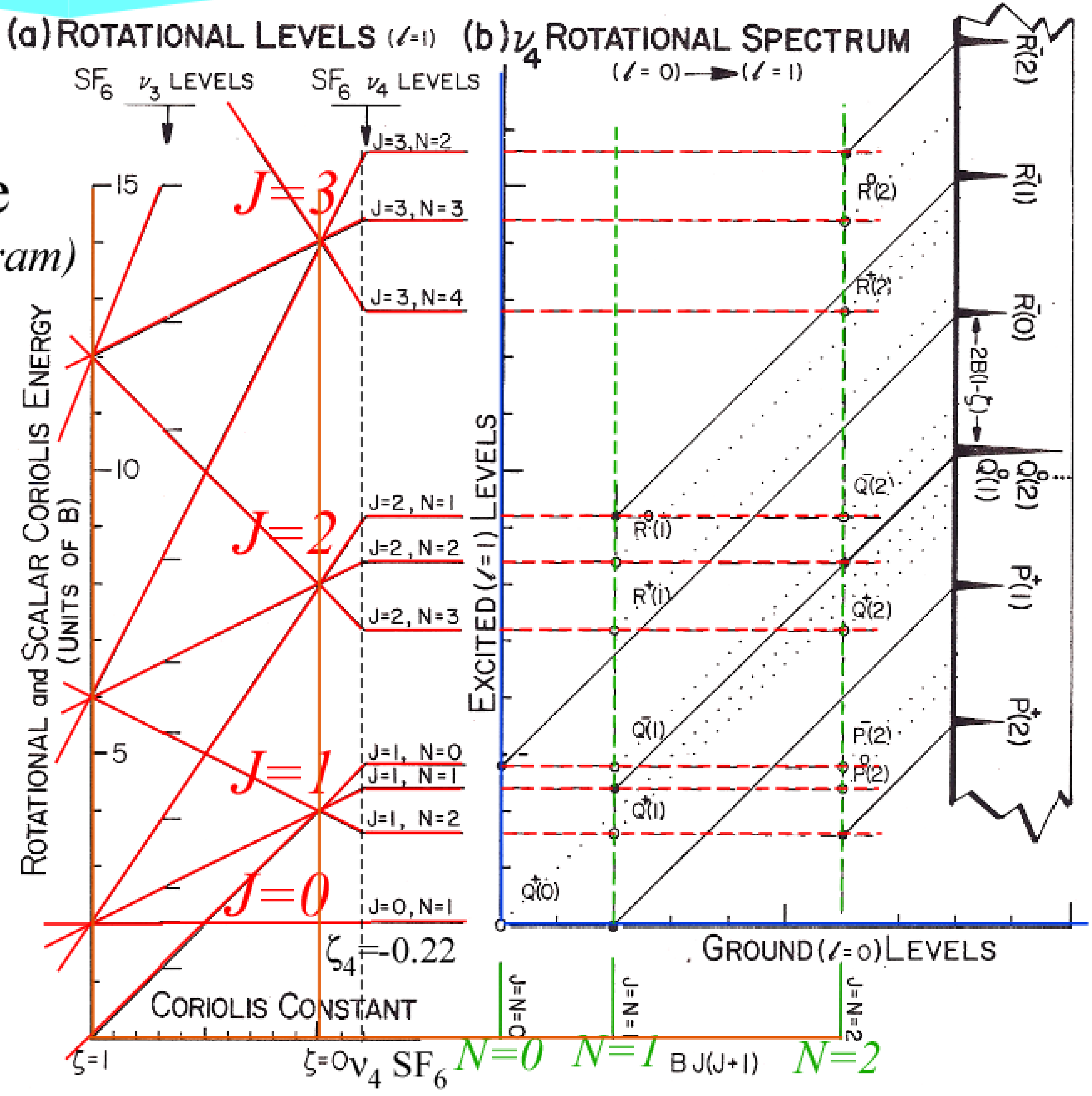
ζ_4=-0.22

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

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

(Using rovib. nomogram)





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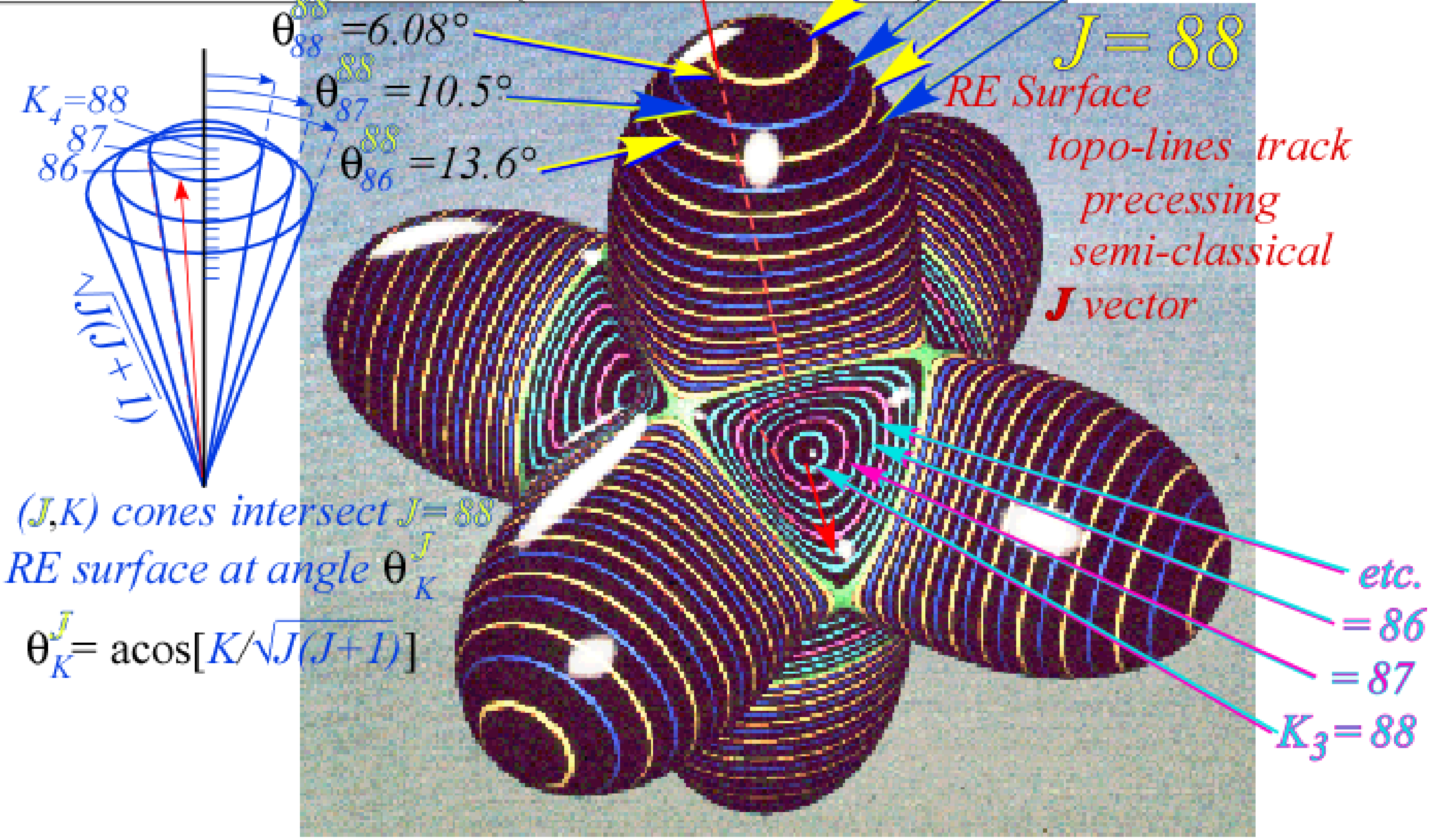
O_h or T_d Spherical Top: *(Hecht CH_4 Hamiltonian 1960)*

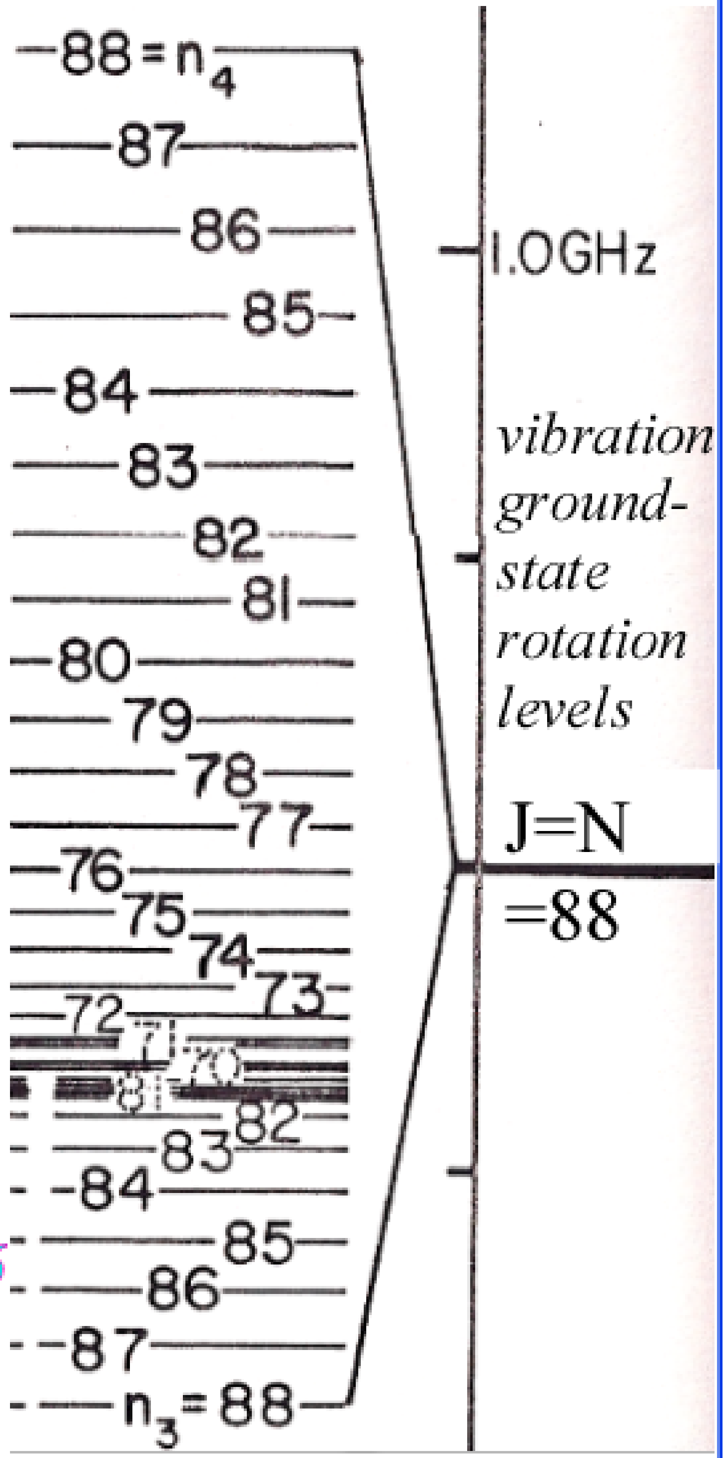
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

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



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

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



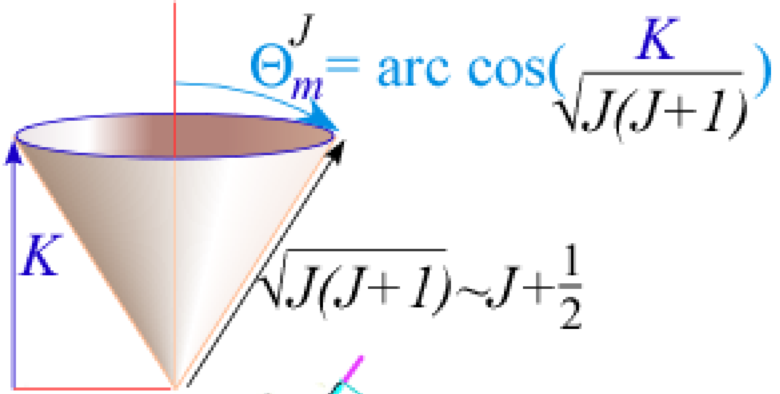
(next page shows slice)

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

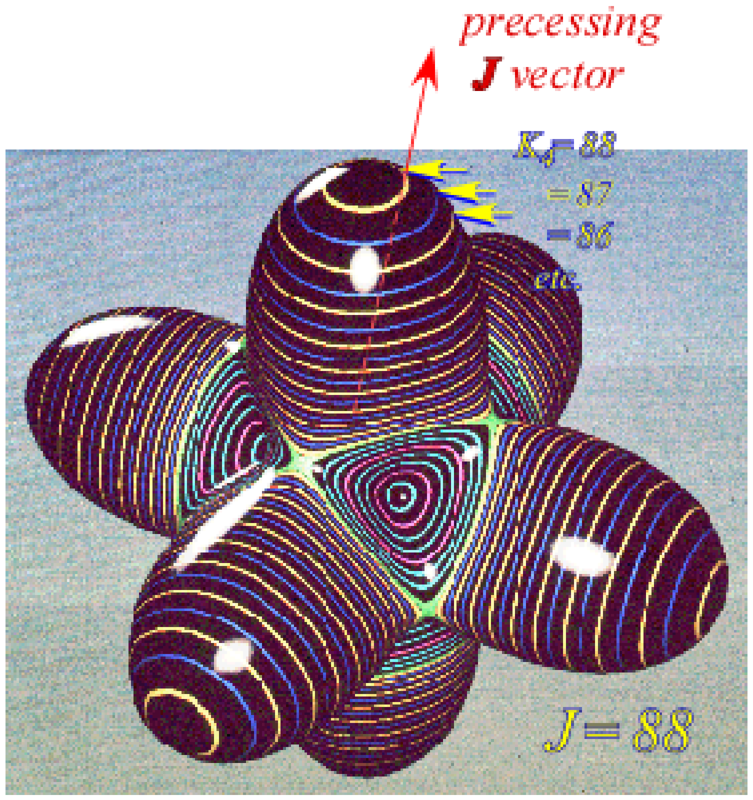
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

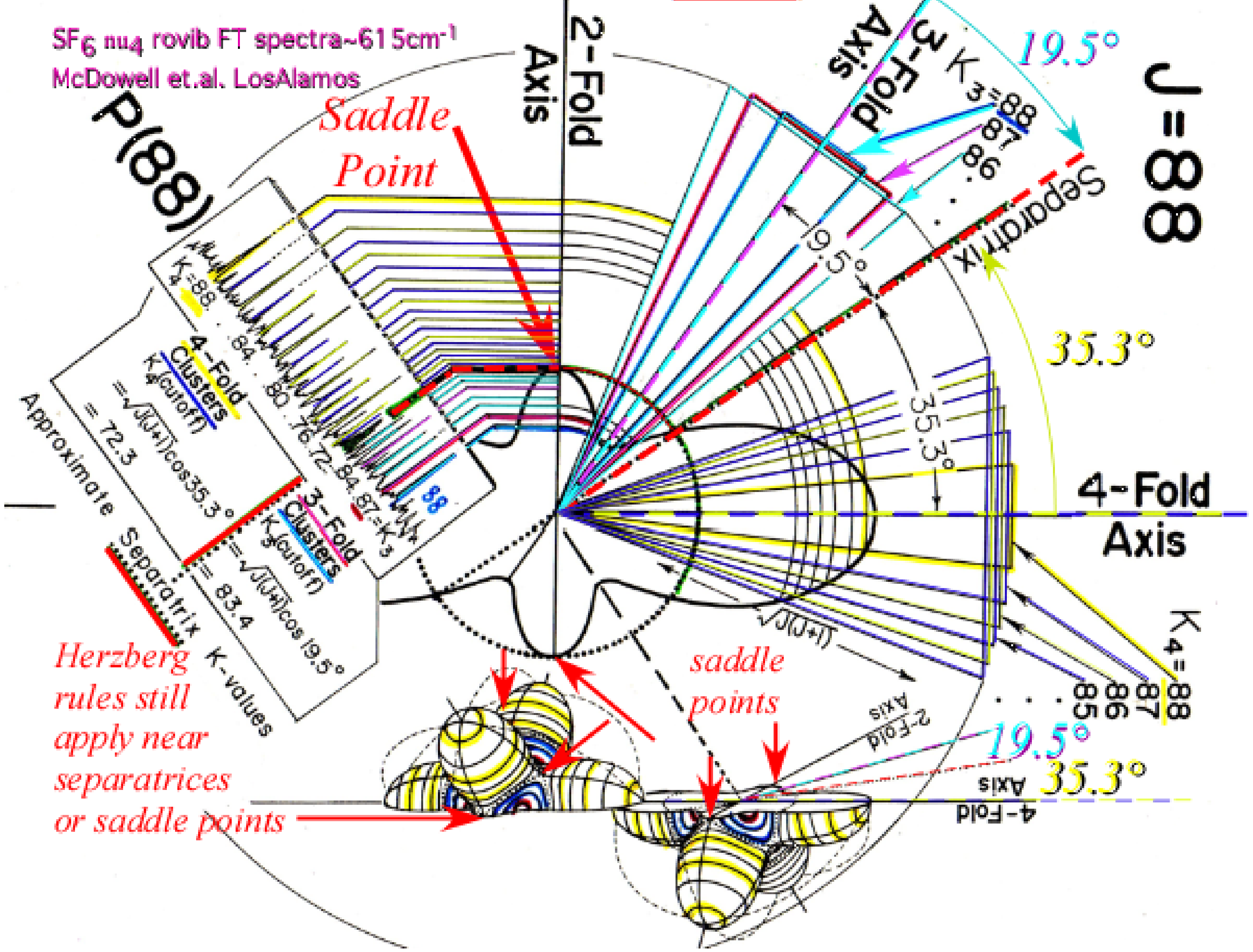
$$= \qquad B\mathbf{J}^2 \qquad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$

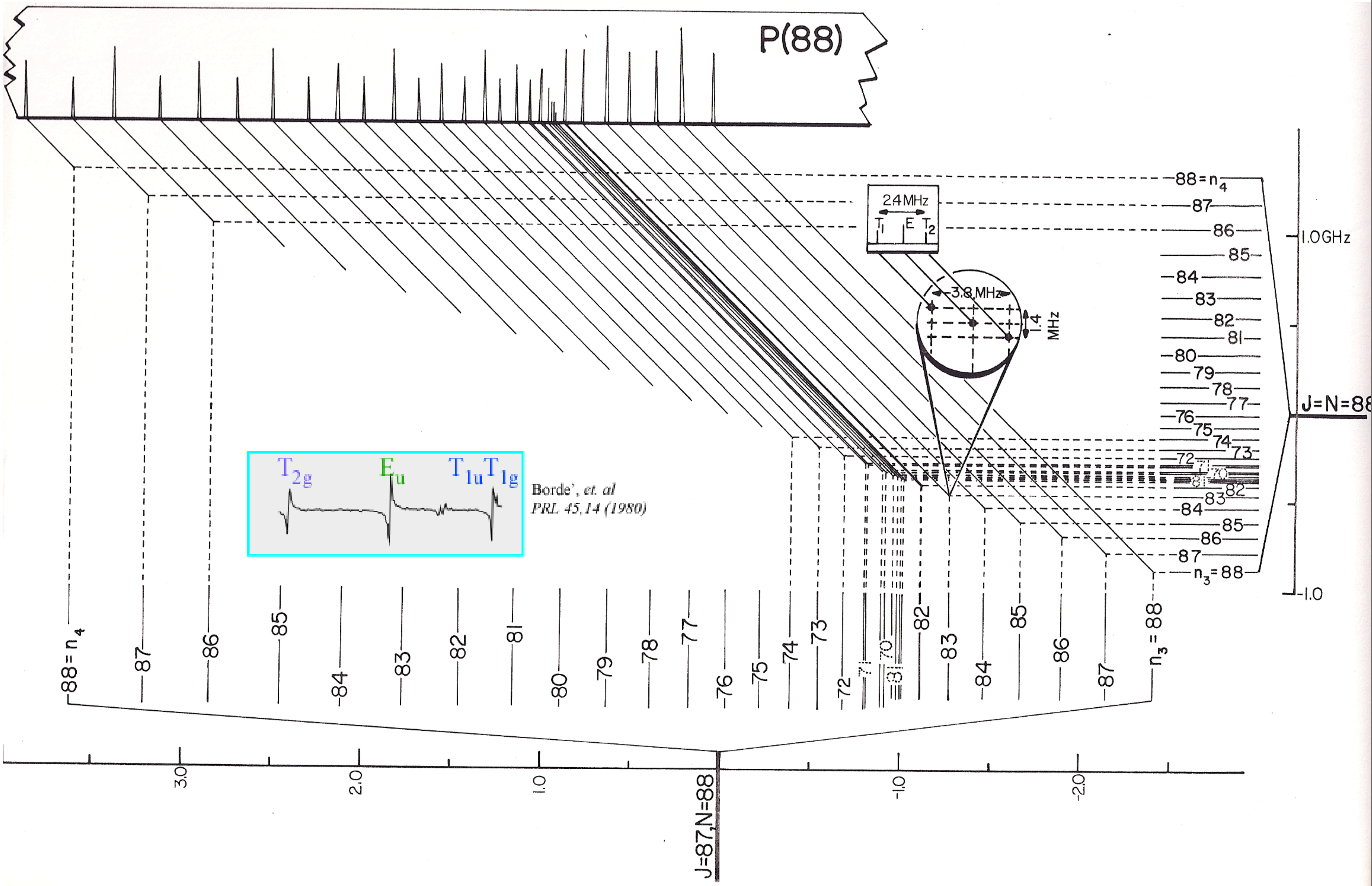
and J-cone intersection



Rovibronic Energy (RE) Tensor Surface







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

Graphical approach to rotation-vibration-spin Hamiltonian

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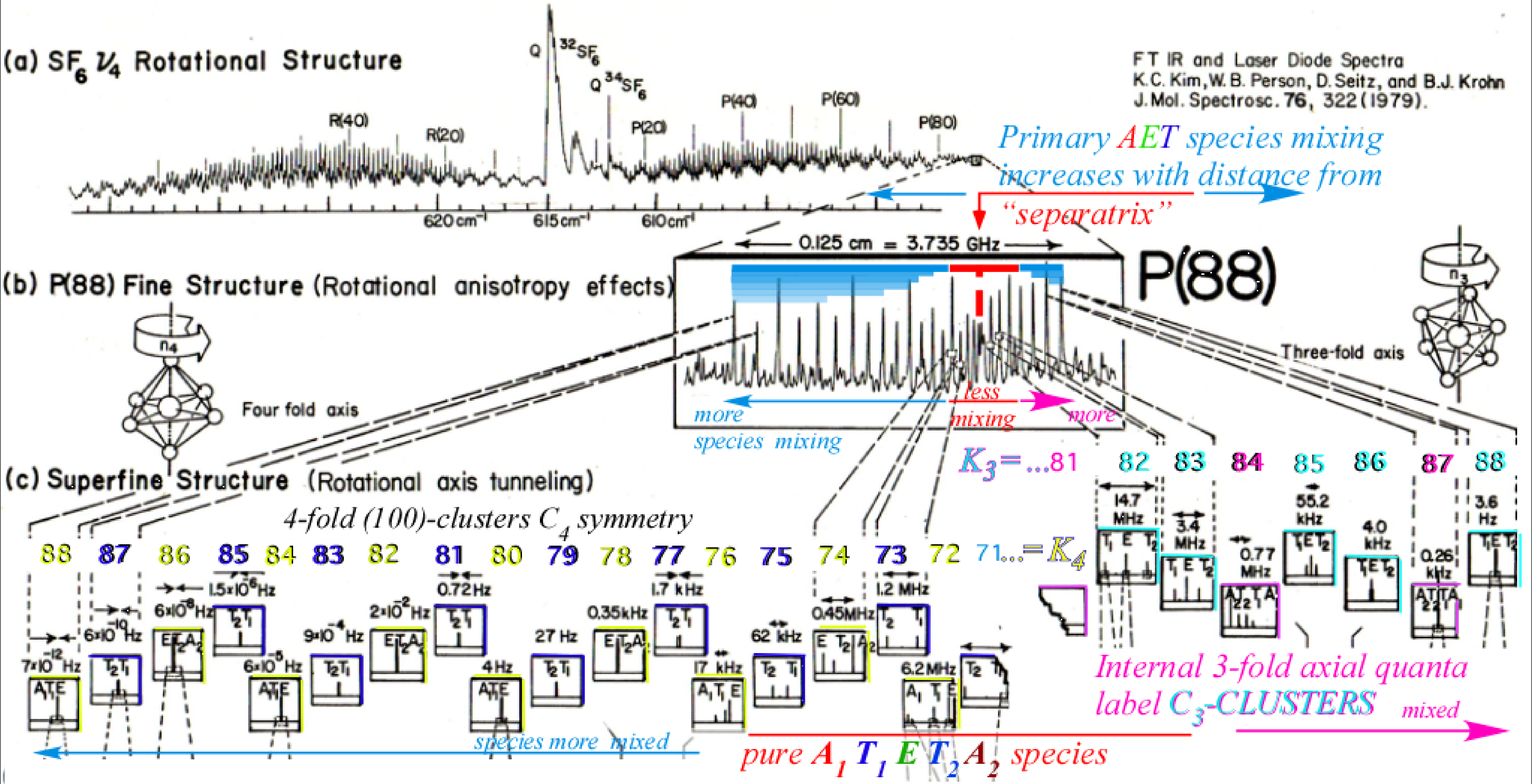
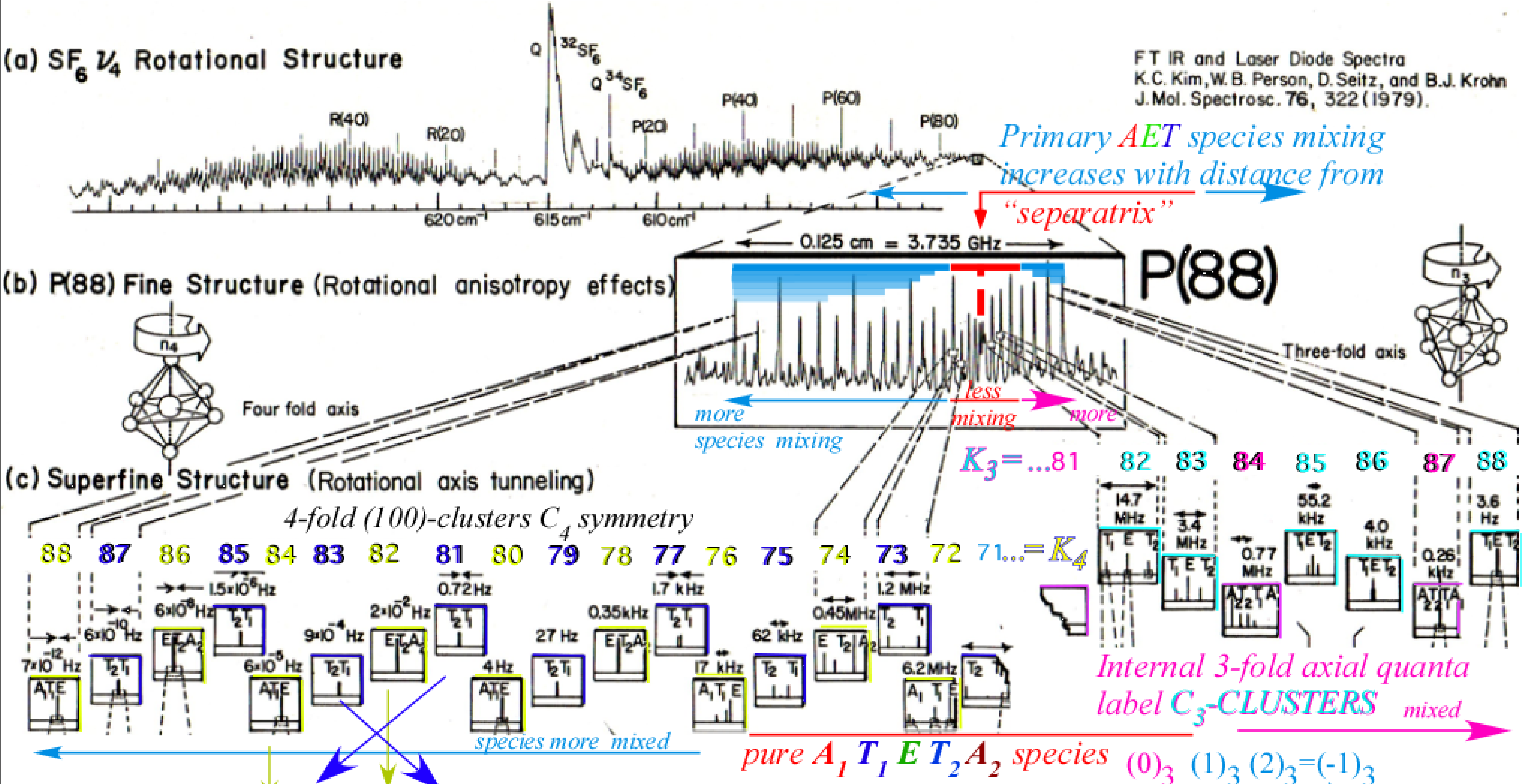

(a) SF6 ν4 Rotational Structure
Q 32SF6
Q 34SF6
R(40)
R(20)
P(20)
P(40)
P(60)
P(80)
620 cm-1
615 cm-1
610 cm-1
FT IR and Laser Diode Spectra
K.C. Kim, W. B. Person, D. Seitz, and B.J. Krohn
J. Mol. Spectrosc. 76, 322 (1979).
Primary AET species mixing increases with distance from "separatrix"
(b) P(88) Fine Structure (Rotational anisotropy effects)
0.125 cm = 3.735 GHz
P(88)
n4
Four fold axis
n3
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
14.7 MHz
3.4 MHz
0.77 MHz
55.2 kHz
4.0 kHz
0.26 kHz
3.6 Hz
T1 E T2
A1 T1 T2 A2
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
A1 T1 E
T2 T1
E T2 A2
Internal 3-fold axial quanta label C3-CLUSTERS
mixed
species more mixed
pure A1 T1 E T2 A2 species



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

more species mixing

less mixing

more

4-fold (100)-clusters C_4 symmetry

Internal 3-fold axial quanta label C_3-CLUSTERS

mixed

species more mixed

pure A_1 T_1 E T_2 A_2 species

	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
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

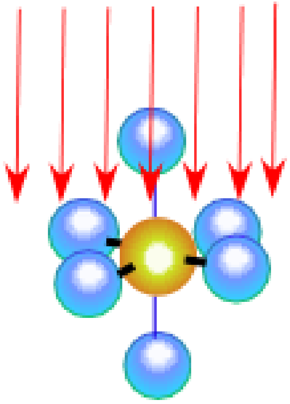
Duality: The "Flip Side" of Symmetry Analysis.

LAB versus BODY, *STATE versus PARTICLE,*

boils down to :

OUTSIDE versus INSIDE

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

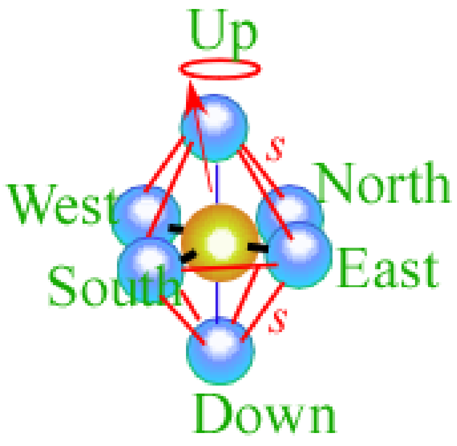


Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

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

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

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



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

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Level or Spectral
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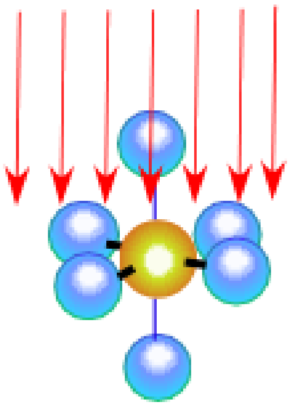

Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

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

INSIDE or BODY
Symmetry reduction
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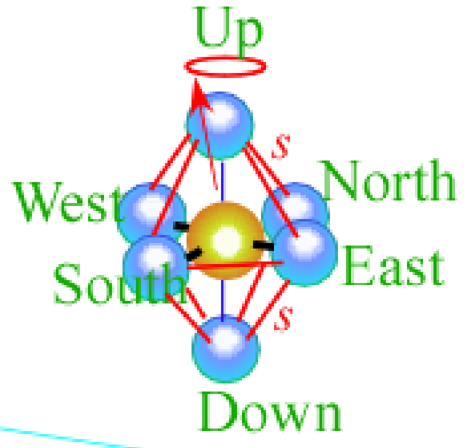
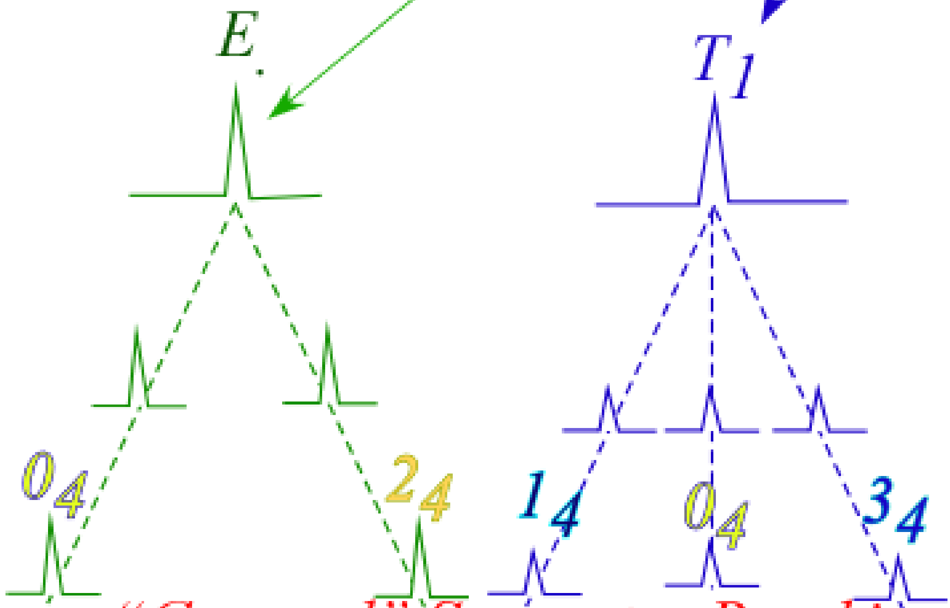
*Internal **J** gets "stuck" on RES axes*
Must "tunnel" axis-to-axis at rate s



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

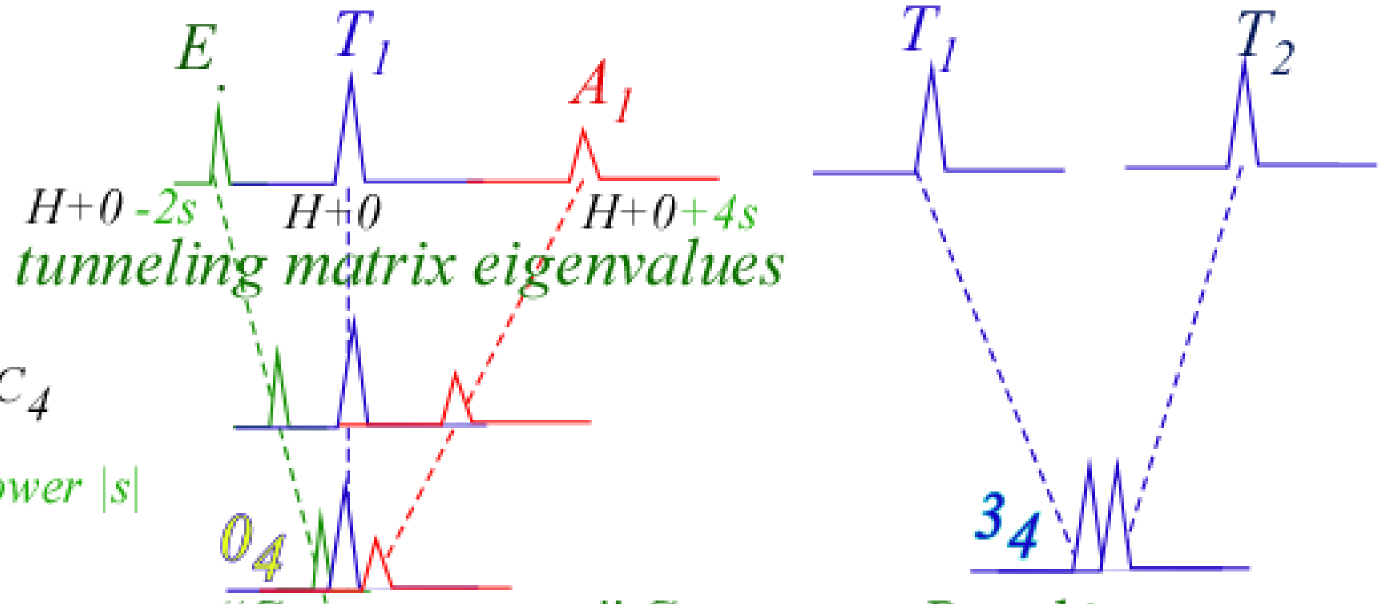
H	0	s	s	s	s
0	H	s	s	s	s
s	s	H	0	s	s
s	s	0	H	s	s
s	s	s	s	H	0
s	s	s	s	0	H



"Coerced" Symmetry Breaking

Stronger C_4

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



"Spontaneous" Symmetry Breaking

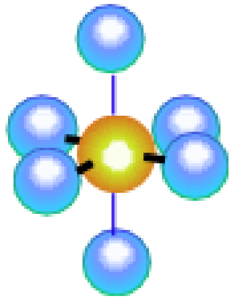
Entanglement!

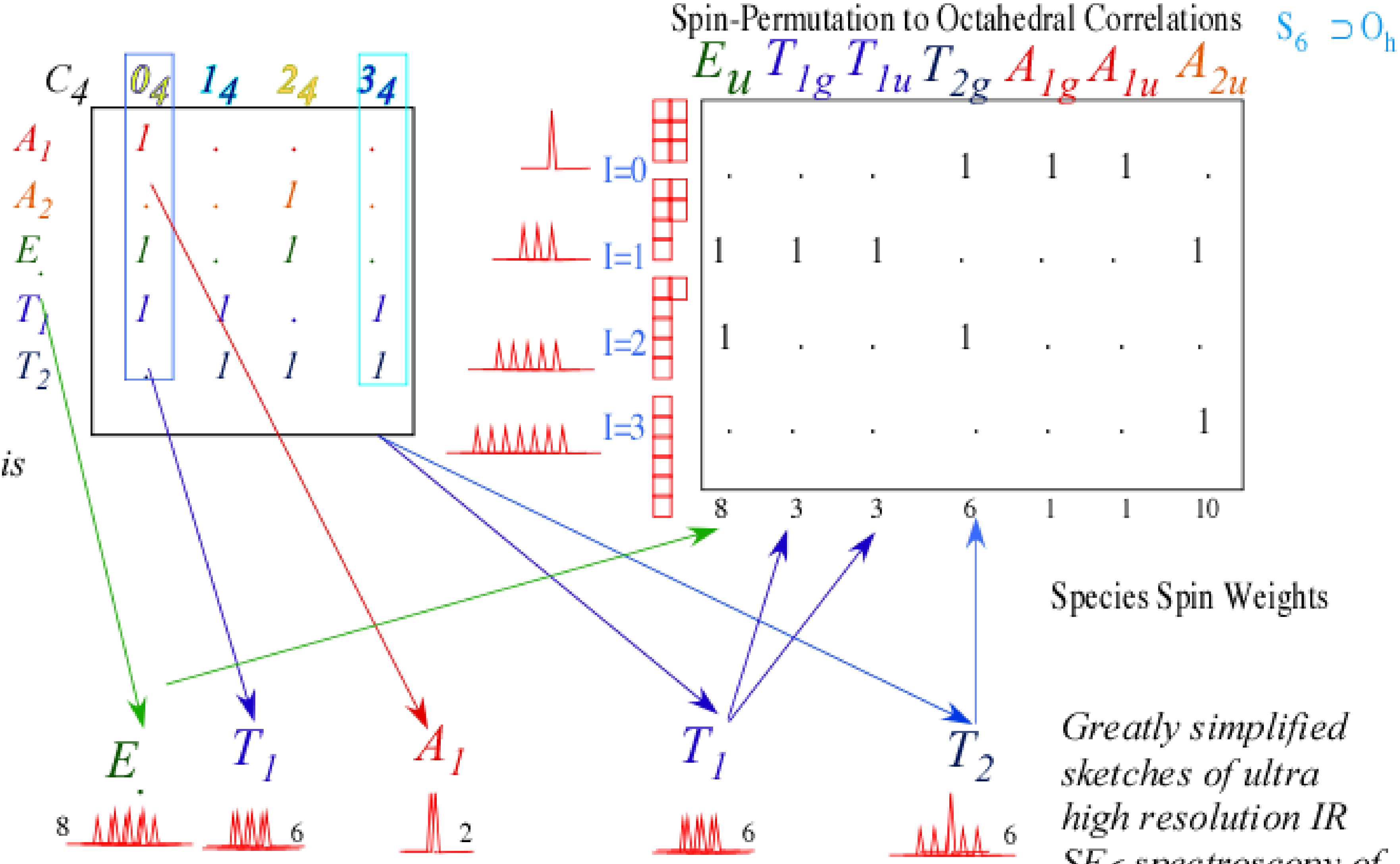
How F-nuclei become distinguished

(but not distinguish__able__)

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

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

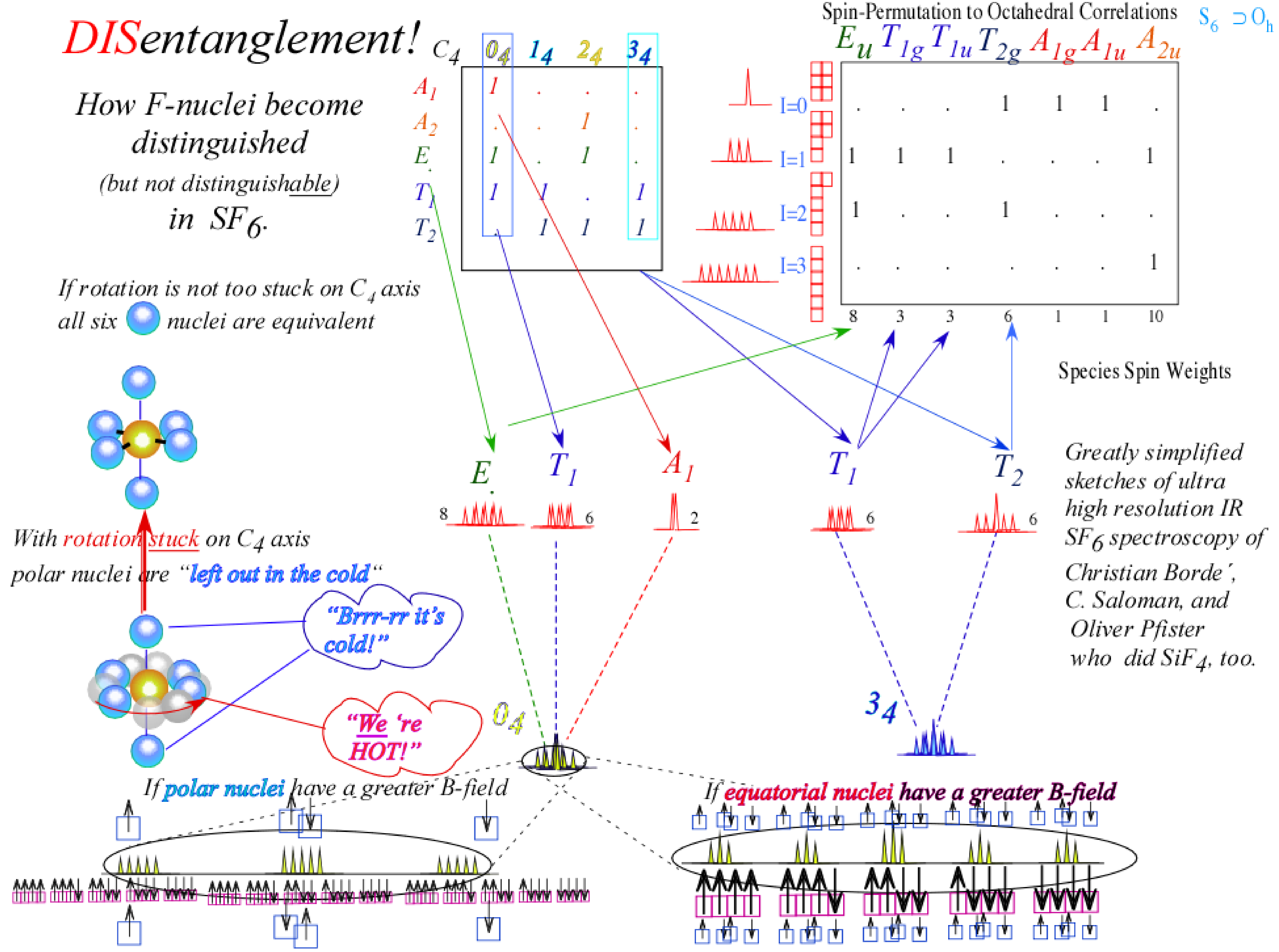
Greatly simplified sketches of ultra high resolution IR SF_6 spectroscopy of Christian Borde´, C. Saloman, and Oliver Pfister who did SiF_4, too.

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

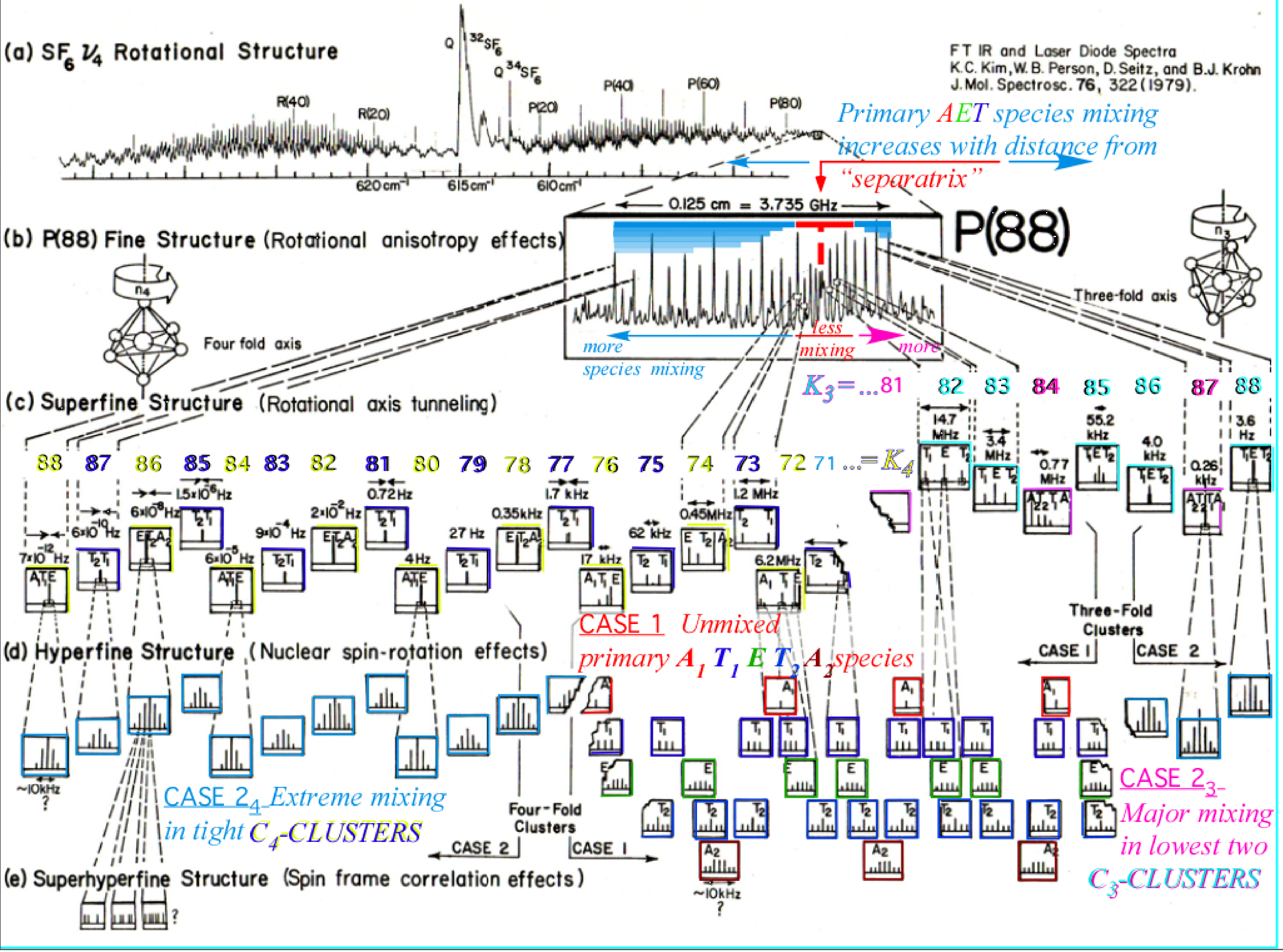
If rotation is not too stuck on C_4 axis all six ● nuclei are equivalent

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

If polar nuclei have a greater B-field

If equatorial nuclei have a greater B-field

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



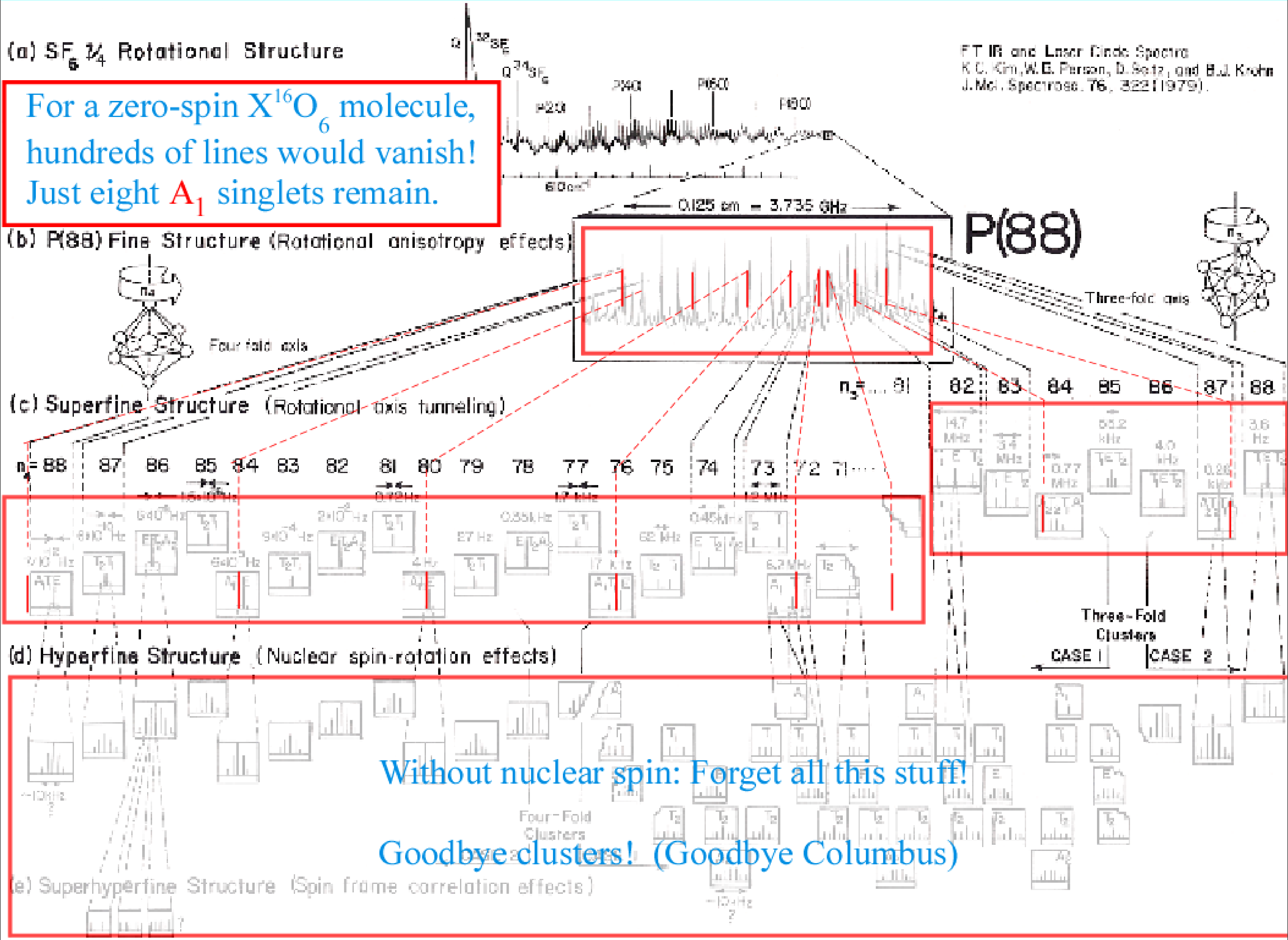
Primary AET species mixing increases with distance from "separatrix"

CASE 1 Unmixed primary A_1 T_1 E T_2 A_2 species

CASE 2_4 Extreme mixing in tight C_4-CLUSTERS

CASE 2_3 Major mixing in lowest two C_3-CLUSTERS

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



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

Without nuclear spin: Forget all this stuff!

Goodbye clusters! (Goodbye Columbus)

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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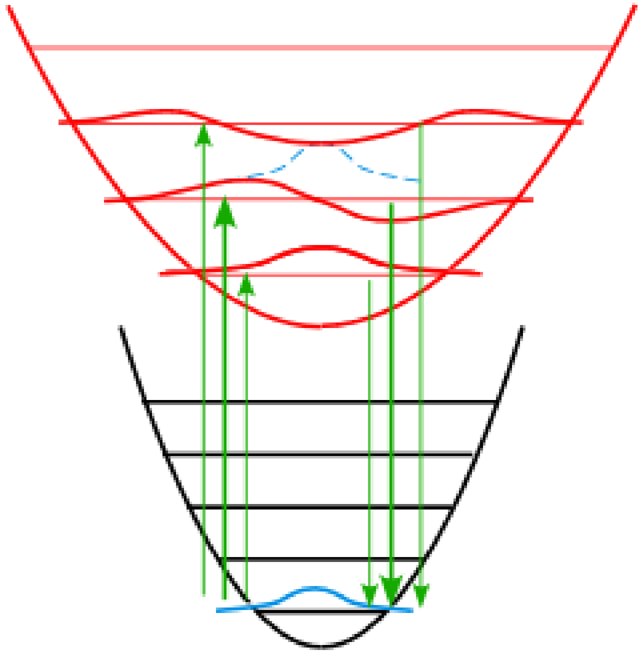
- *Rotational Energy Eigenvalue Surfaces (REES)* — ν_3 SF_6

Potenial Energy Surface (PES) Dynamics

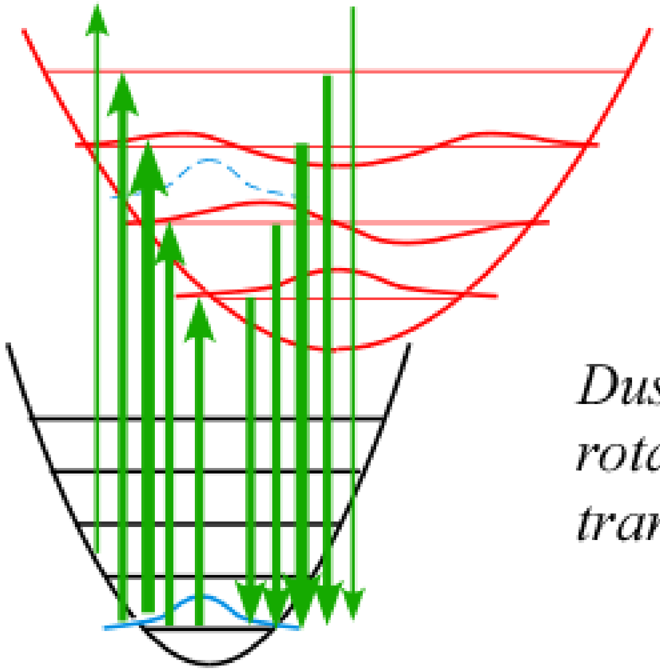
Inter-PES electronic transitions

Vibrational Franck-Condon effects

- Frequency mismatch of PES



- Shape or position mismatch of PES



Duschinsky rotation or translation

Analogy between

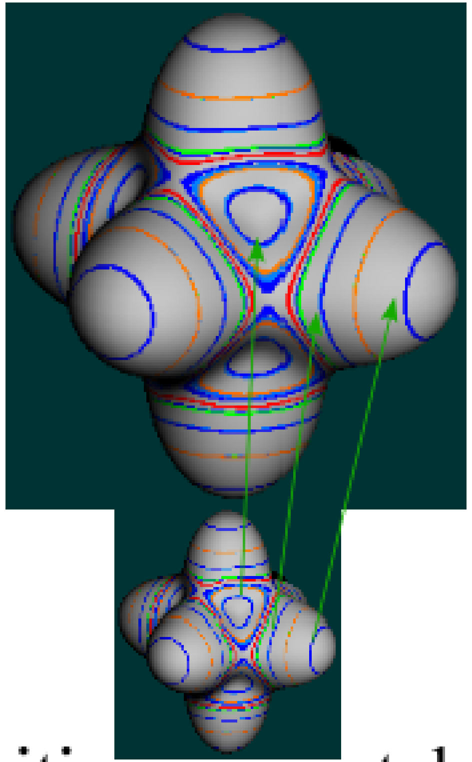
Vibronic and Rovibronic

Rotation Energy Surface (RES) Dynamics

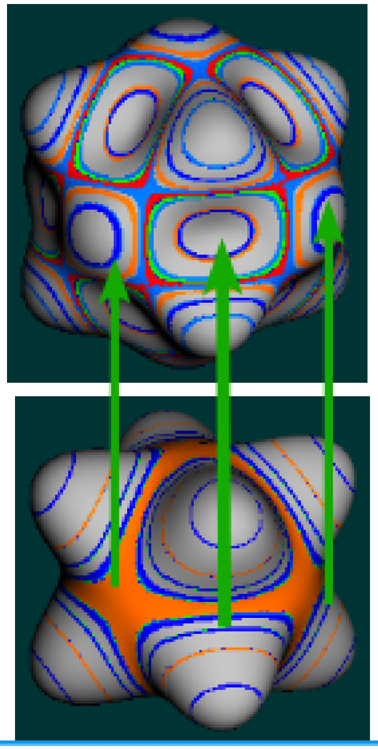
Inter-PES electronic transitions

Rotational "Franck-Condon" effects

- Frequency mismatch of RES



- Shape or position mismatch of RES

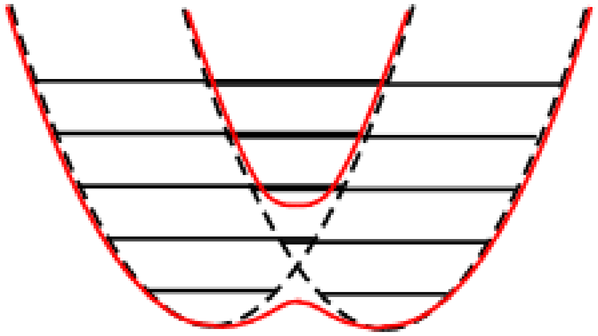


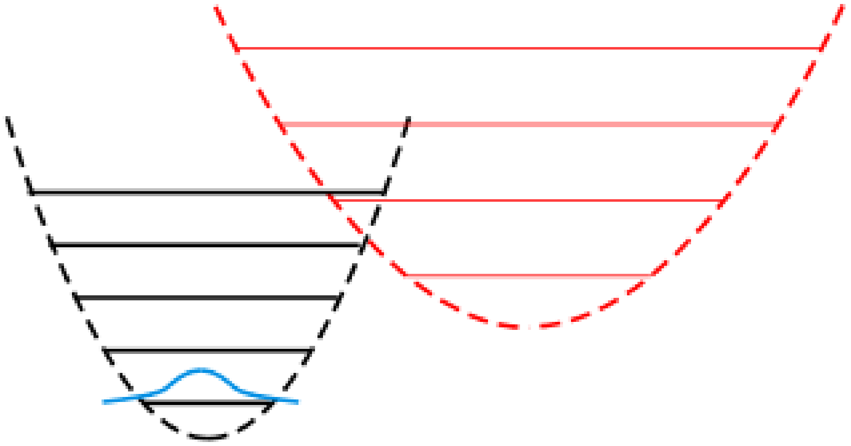
Non-Born-Oppenheimer Surfaces

Strong vibration-electronic mixing

Jahn-Teller-Renner effects

- Multiple and variable conformer minima





Rotation Energy Eigen-Surfaces (REES)

Inter-PES electronic transitions

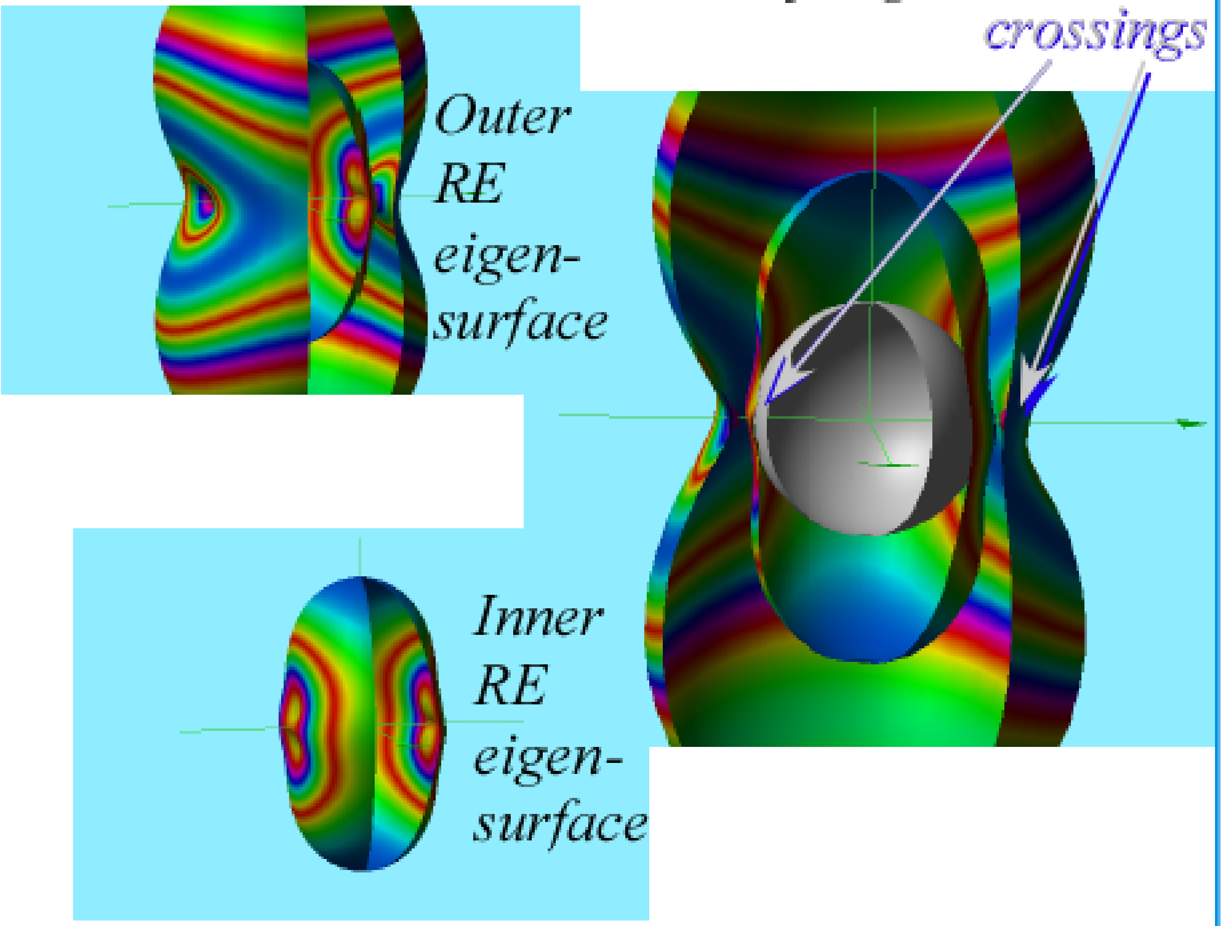
Rotational JTR effects

- Multiple and variable J-axes

Analogy between

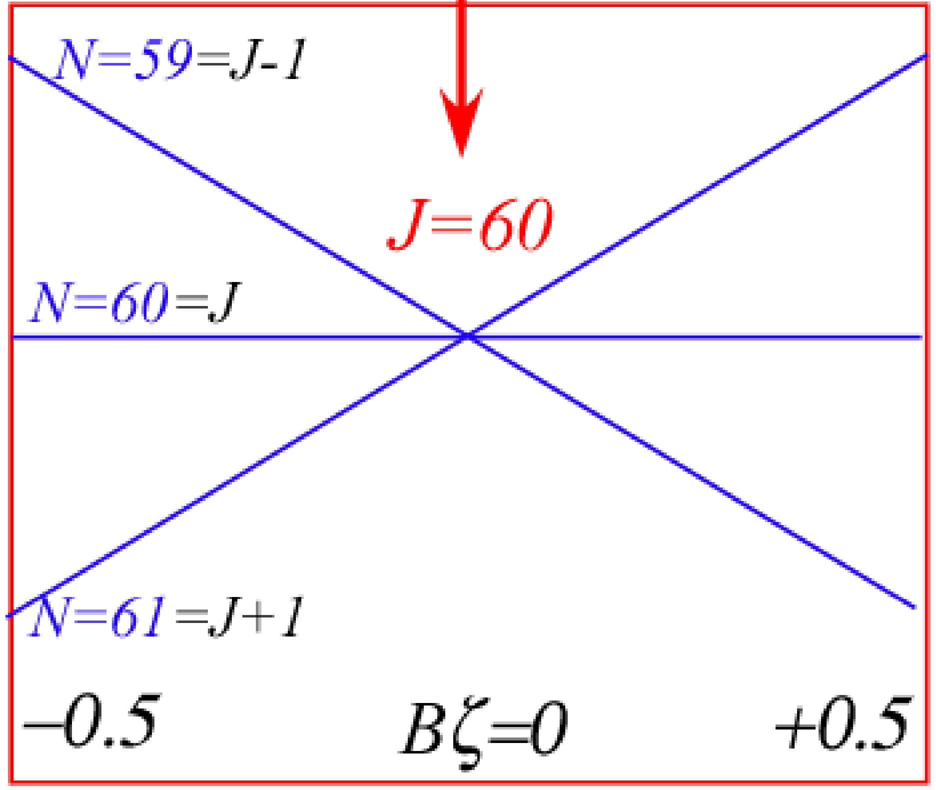
Vibronic and Rovibronic

Example for 2-state vibronic-rotor coupling



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

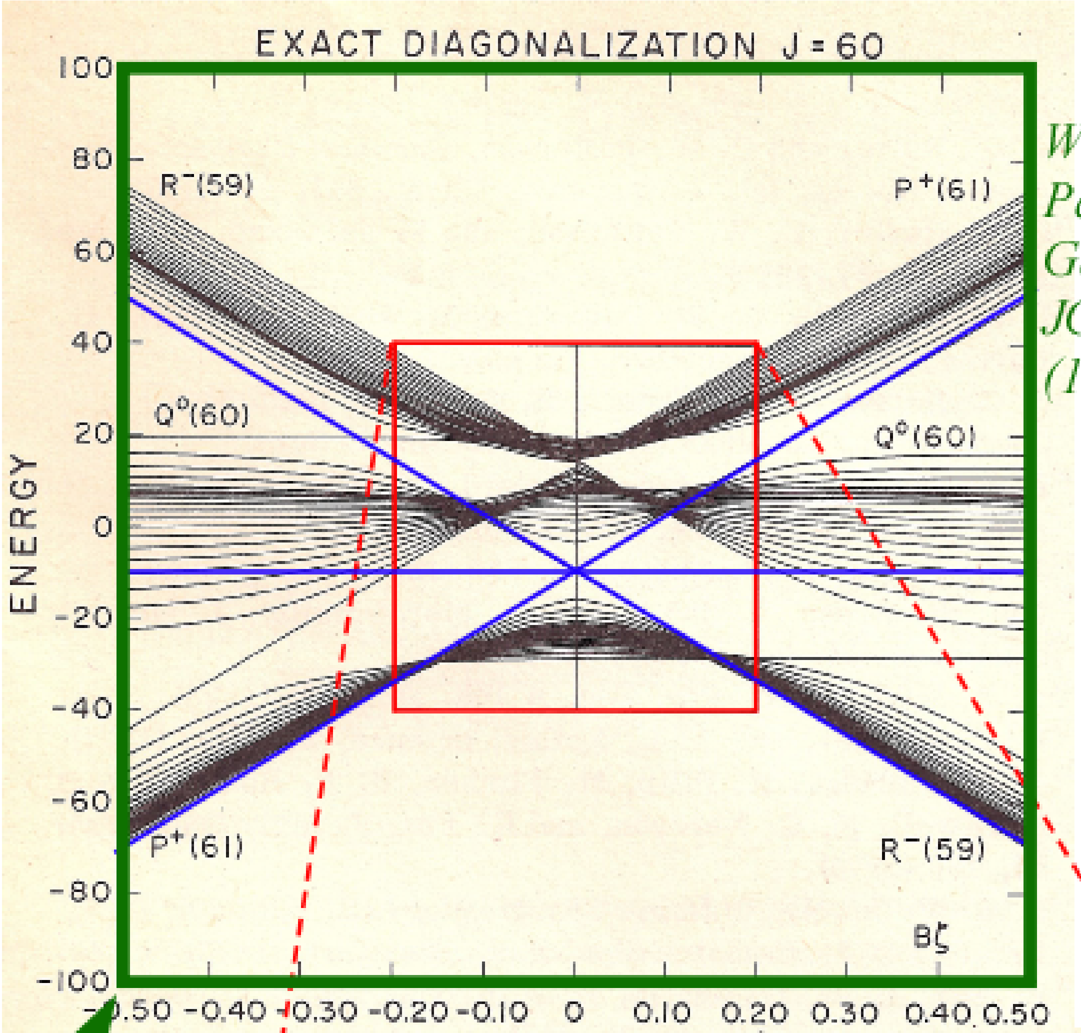
Here is a $J=60$ piece of it:



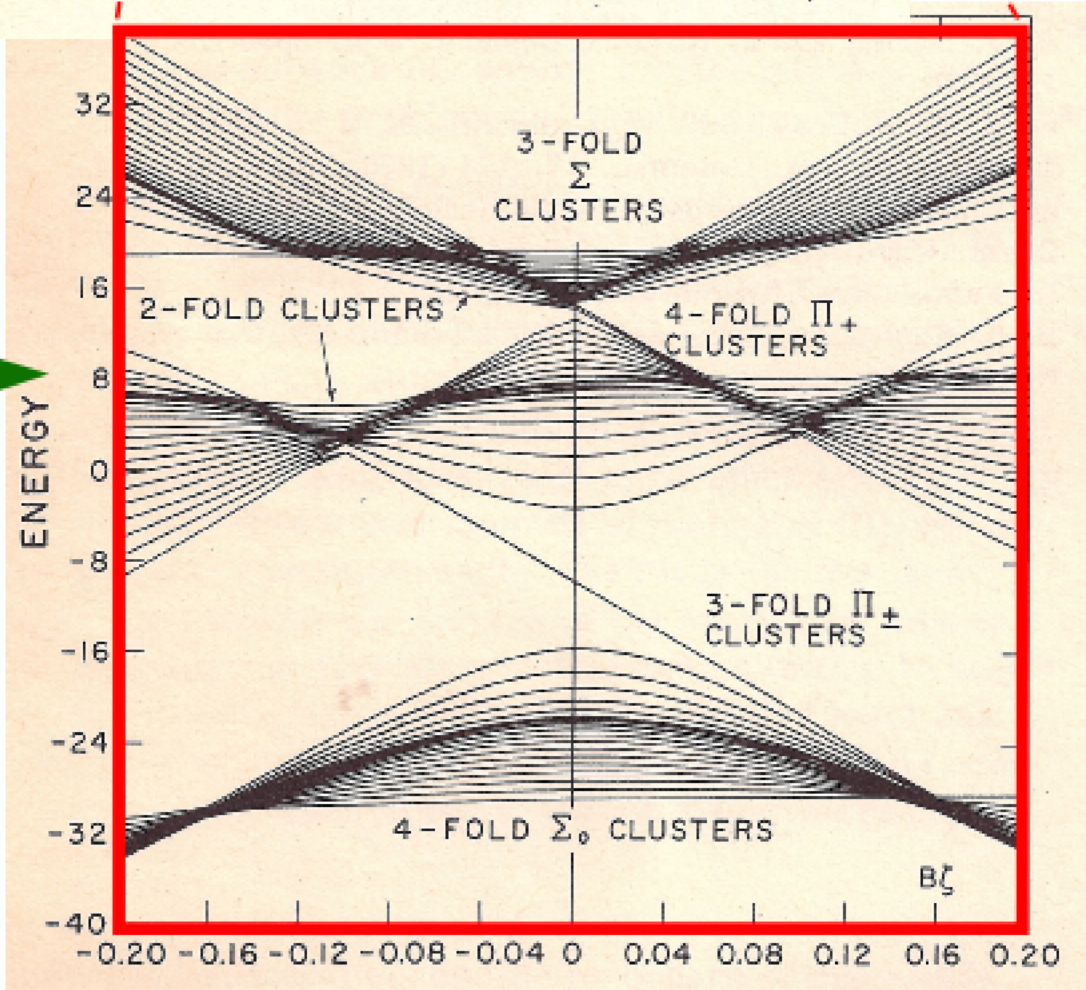
Now consider this plot with *tensor* Coriolis, too

(Just 4th-rank $[2\text{x}2]^4$ tensor here.

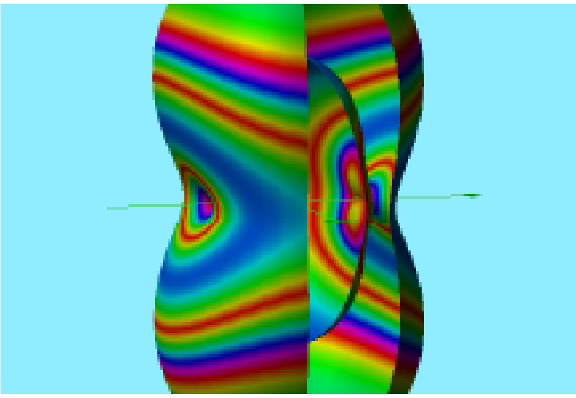
See next talk **RJ06** and a 4PM talk **RI09** by ***Mitchell** et. al.* and ***Boudon** et. al.* who will pull much higher rank!)



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



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



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

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

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

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

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

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

Body-ΣΠ±-Basis

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

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

Lab-PQR-Basis

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

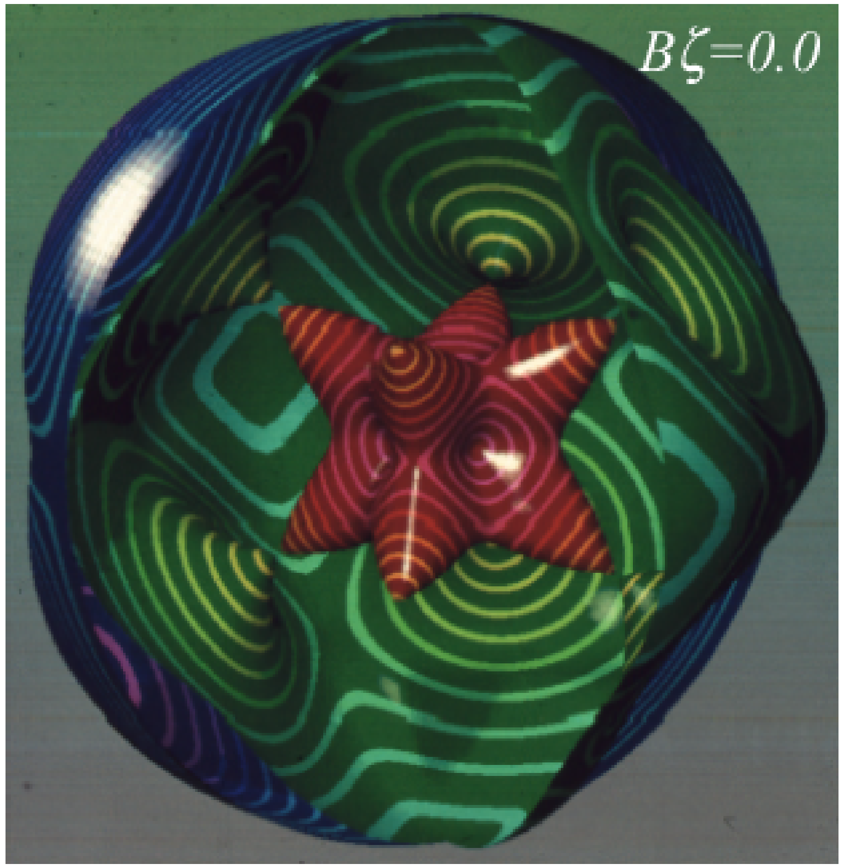
(Either basis should give same REES)

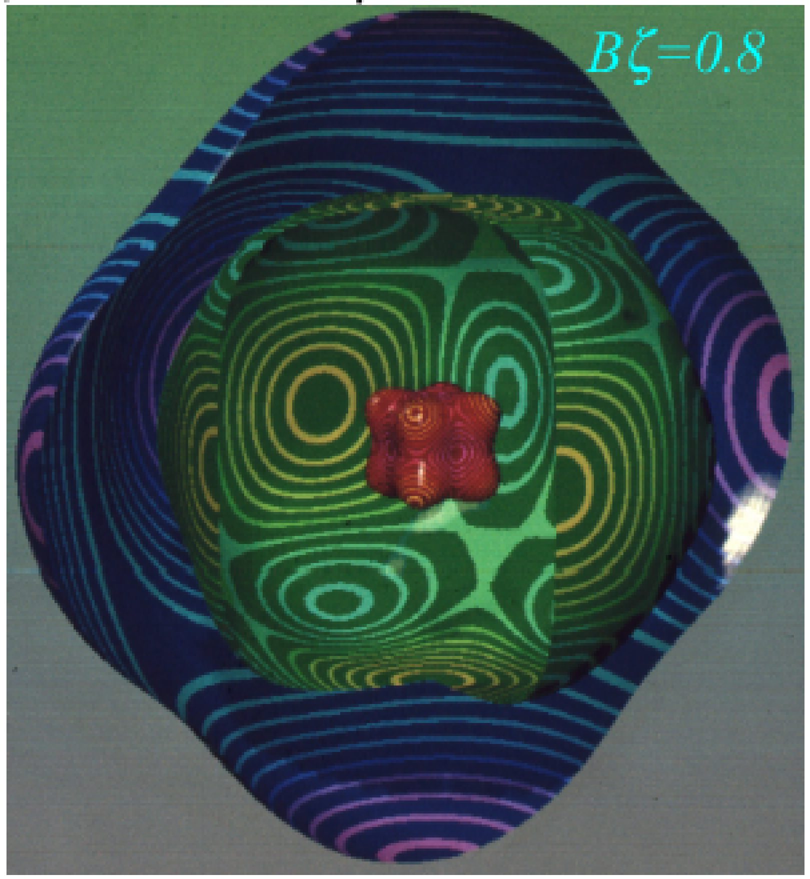
$$+2t_{224}|J|^2\begin{pmatrix}H_{PP}&H_{PQ}&H_{PR}\\H^*_{PQ}&H_{QQ}&H_{QR}\\H^*_{RP}&H^*_{QR}&H_{RR}\end{pmatrix}$$

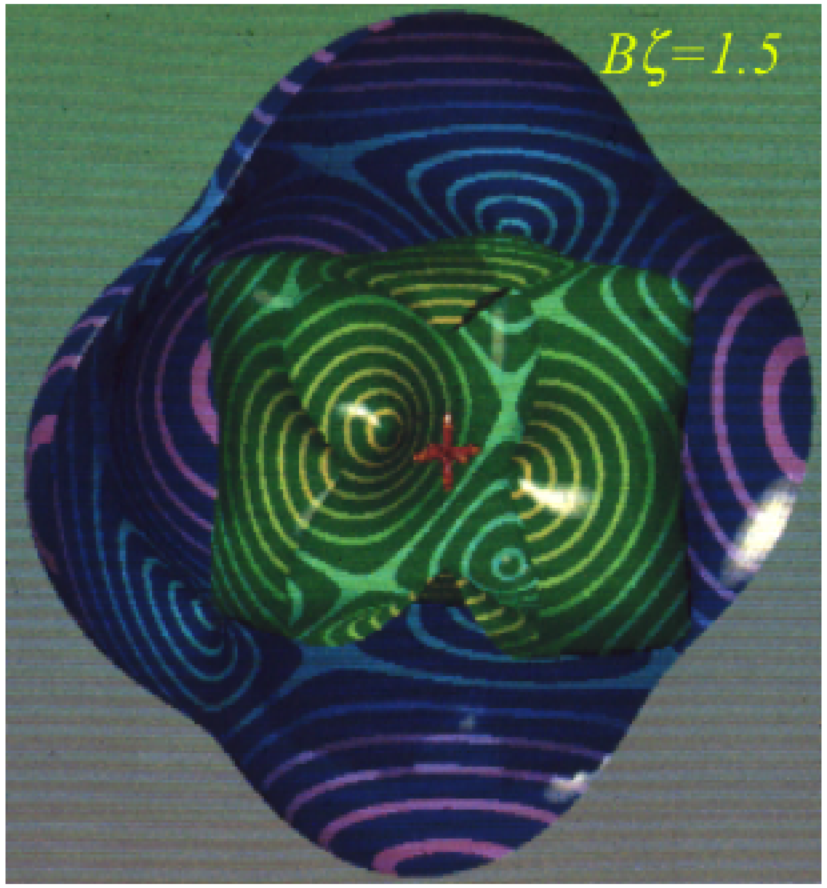
$$H_{PP}=(35\cos^4\beta-30\cos^2\beta+5\sin^2\beta\sin4\gamma+5)/4=H_{RR}$$

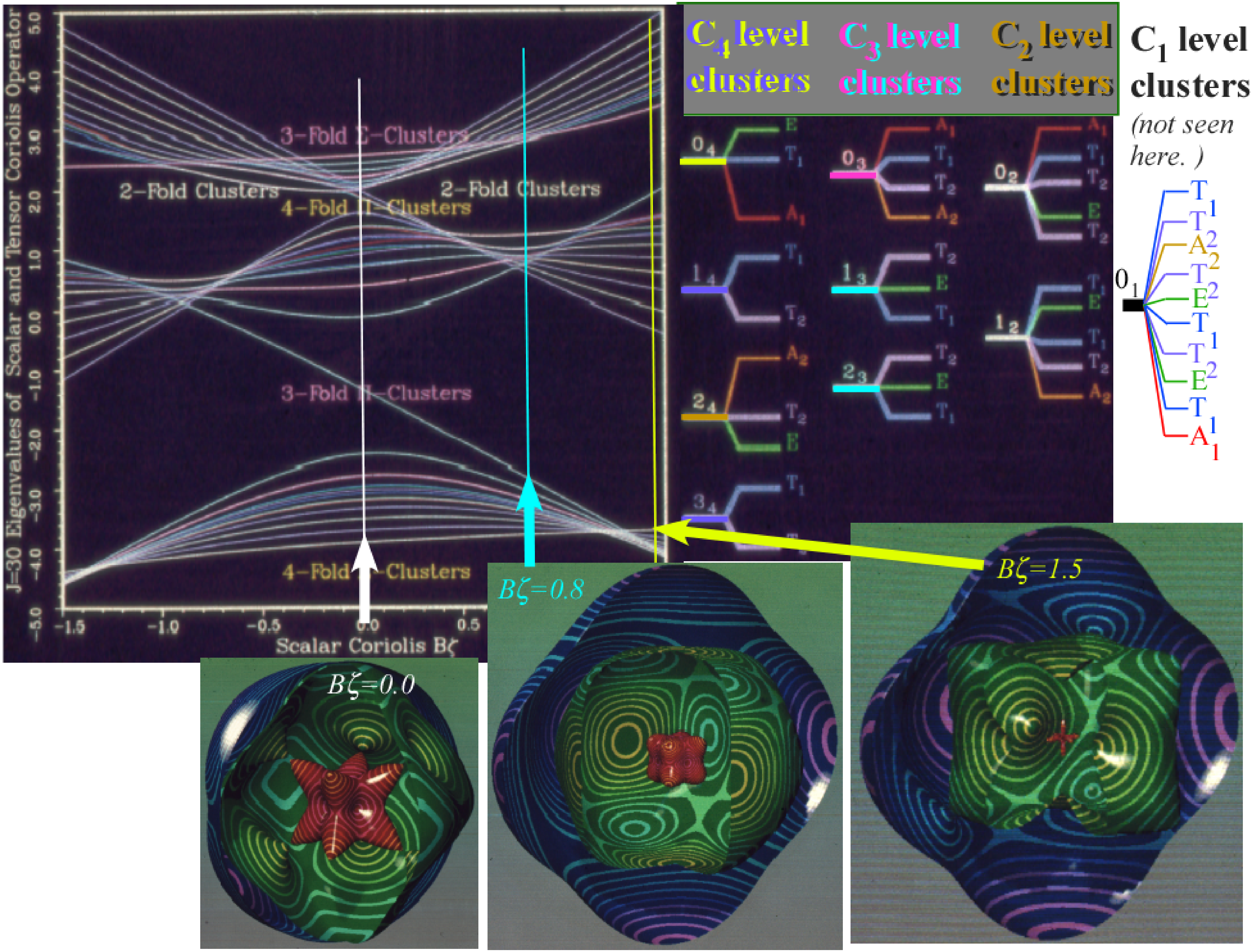
$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

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







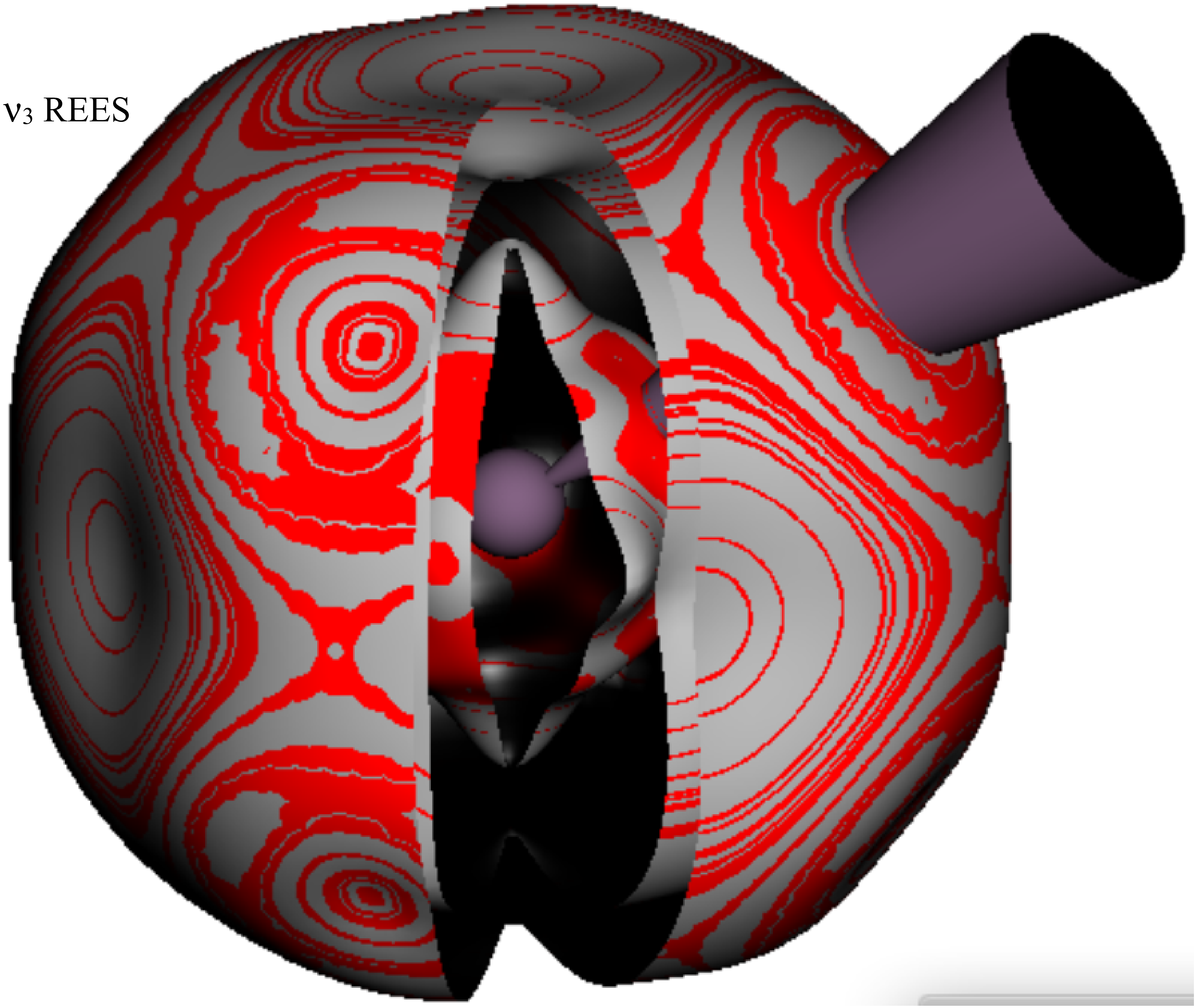


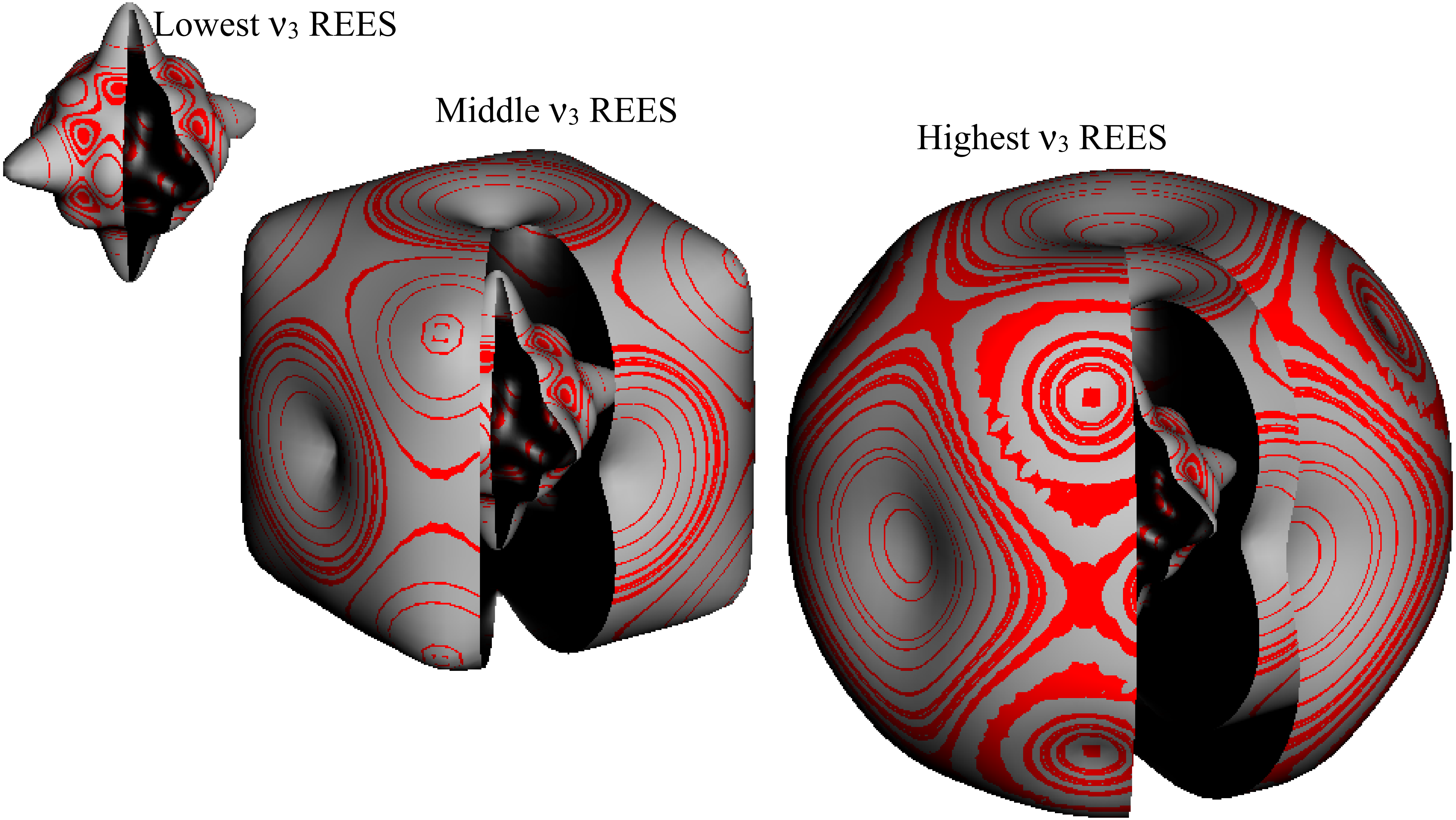
C_4 level clusters **C_3 level clusters** **C_2 level clusters**

C_1 level clusters

(not seen here.)

ν_3 REES





Lowest ν_3 REES

Middle ν_3 REES

Highest ν_3 REES

New geometric approach to rotational eigenstates and spectra

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

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

W.G.Harter

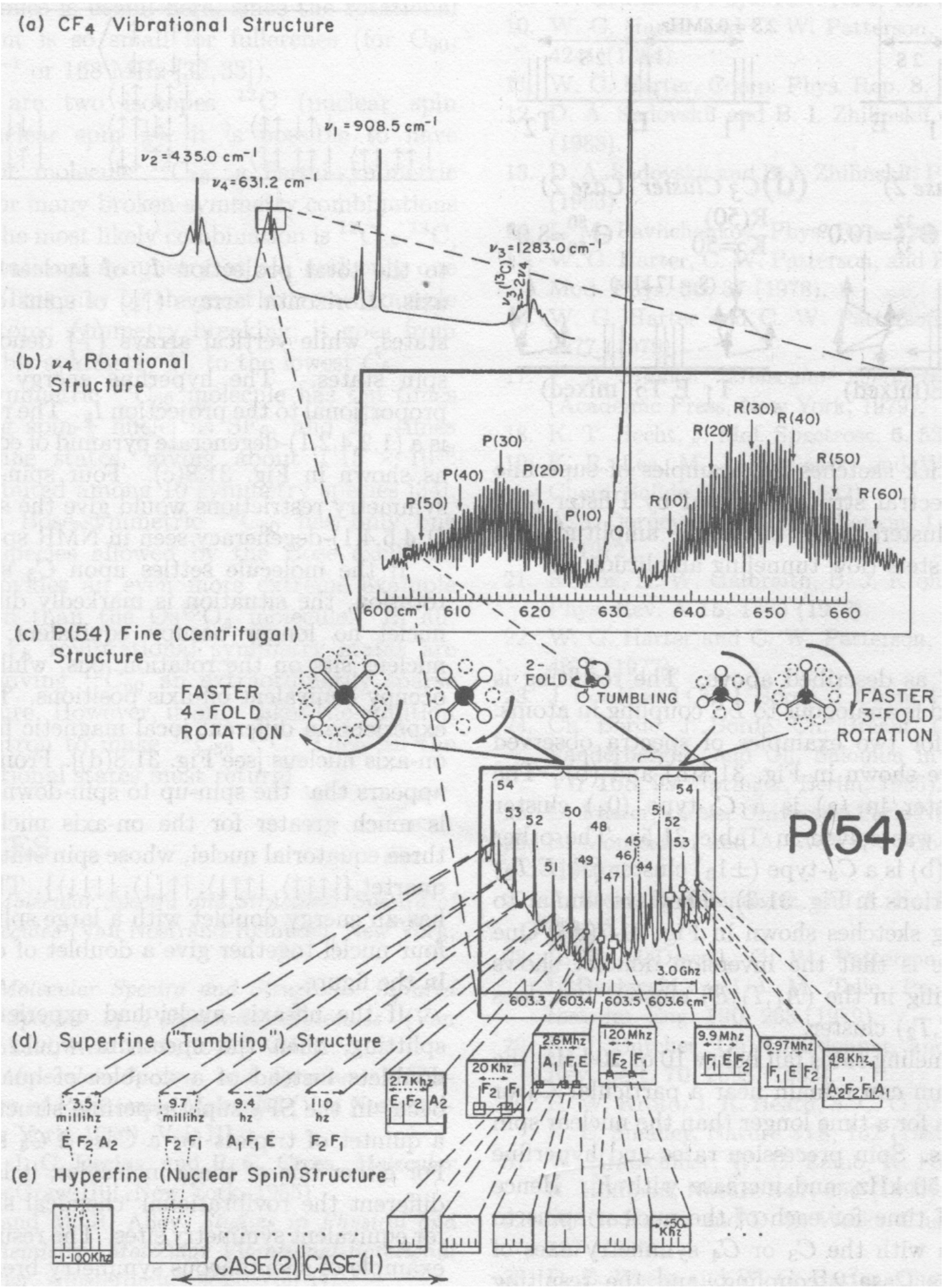
Ch. 31

Atomic, Molecular, & Optical Physics Handbook

Am. Int. of Physics

Gordon Drake Editor

(1996)



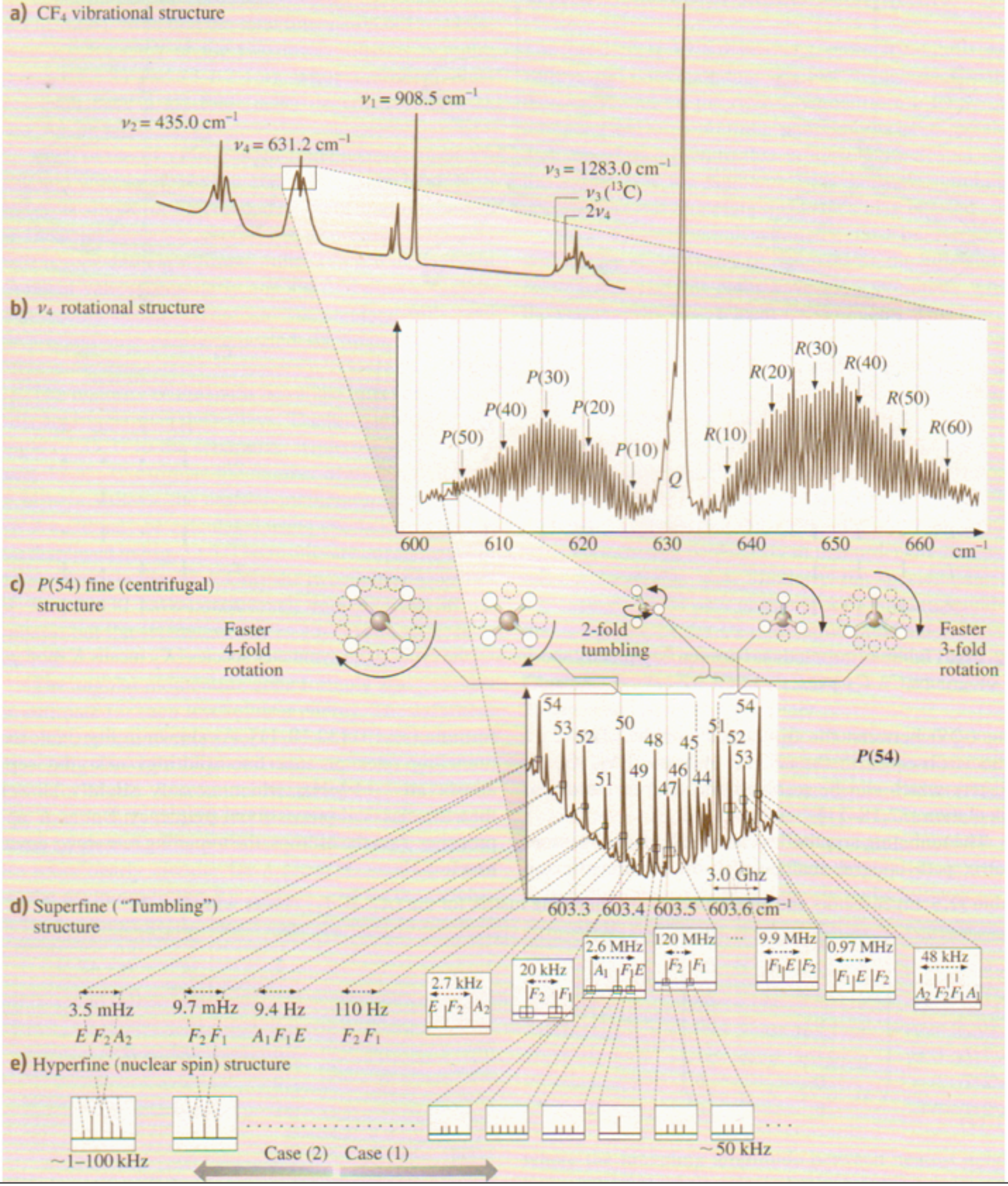
Example of frequency hierarchy for 16μm spectra of CF_4 (Freon-14)

W.G.Harter

Fig. 32.7

Springer Handbook of Atomic, Molecular, & Optical Physics

Gordon Drake Editor (2005)



As of April 3, 2014

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

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

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

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

Individual web-apps for current classes:

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

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

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

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

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

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