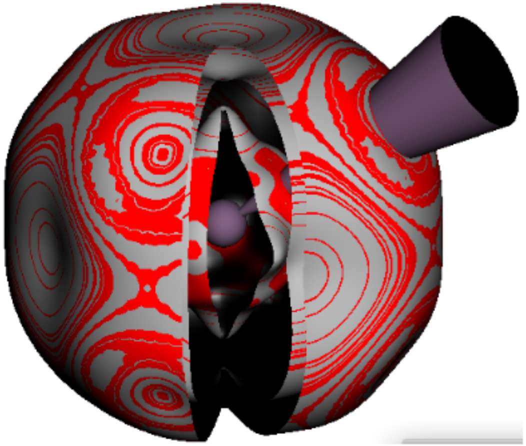
ENERGY-LEVEL-CLUSTER RELATED NUCLEAR-SPIN EFFECTS AND SUPER-HYPERFINE SPECTRAL PATTERNS: HOW MOLECULES DO SELF-NMR:

internal-rotor molecules and spin symmetry conversion effects

William G. Harter and Justin C. Mitchell
Department of Physics, University of Arkansas
Fayetteville, AR 72701

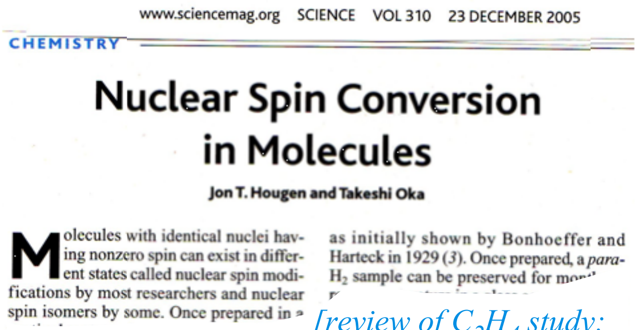


CONSERVATION OF ROVIBRONIC SPECIES - Two Views:

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

*[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***...”*

...for diatomic molecules...I p. 150

...for D_2 asymmetric tops...II p.468

...for D_n symmetric tops...II p.415

...for O-T_d spherical tops...II p.441-453

...during transitions involving...

- *...rotational states,...III p.246*
- *...vibrational states,... ” ”*
- *... electronic states,... ” ”*
- *... collisional states... ” ”*

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

Conservation and preservation?

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

Conversion, perversion or transition?

CONSERVATION OF ROVIBRONIC SPECIES - *Two Views:*

Old

(1939, 1945, and 1966)

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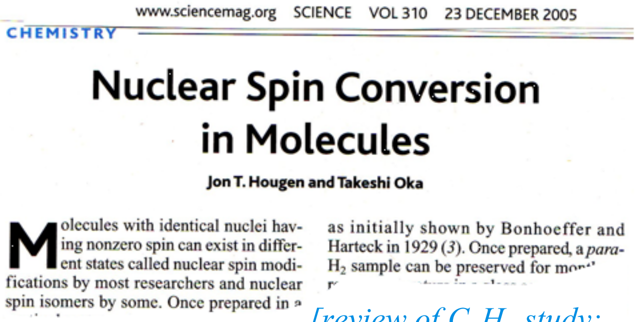

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Strictly *versus* ***NOT!***

Conservation and
preservation?

To conserve vs. To convert

To preserve vs. To pervert

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

Conversion, perversion
or transition?

perversion

Widespread and extreme mixing of species
reported in CF4, SiF_4 and SF_6 :

Ch. Borde, Phys. Rev. ***A20****,254(1978)(expt.)*
Harter, Phys. Rev. ***A24****,192 (1981)(theory)*

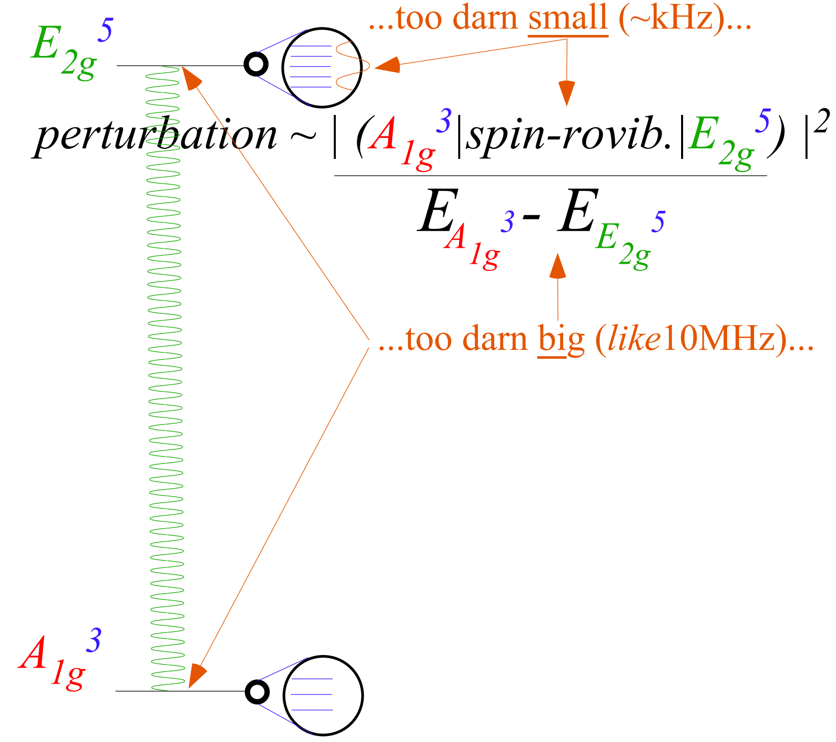
HOW **CONSERVED** IS ROVIBRONIC-SPIN SYMMETRY?

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

A_{2u}^{1}

No Way!

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



E_{2g}^{5}

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

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

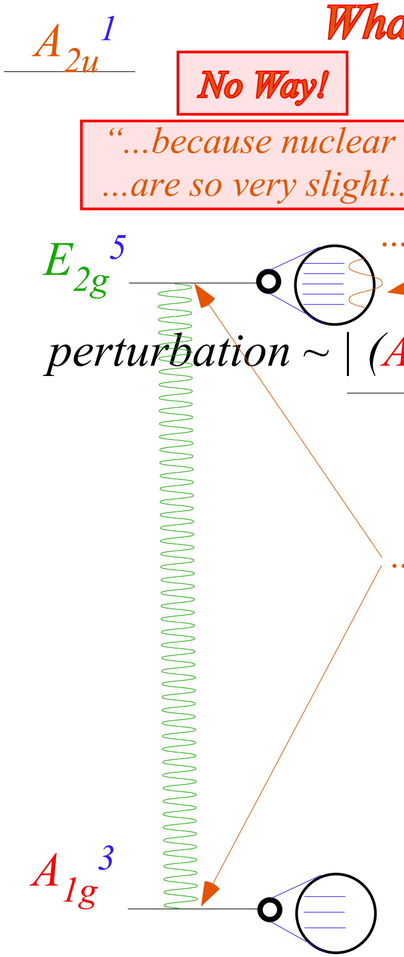
...too darn big (*like*10MHz)...

A_{1g}^{3}

or perverted?

HOW CONSERVED IS ROVIBRONIC-SPIN SYMMETRY?

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



No Way!

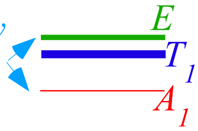
"...because nuclear moments...
...are so very slight..."

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

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

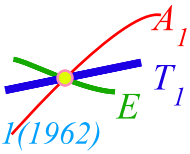
...too darn big (*like*10MHz)...

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



WAY!

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



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

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

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

RE Superhyperfine transitions
Hyperfine effects may rule! 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)

$\nu_3/2\nu_4$ *See* **RJ06 & RI09**

Symmetry-level-cluster effects in SF_6, SiF_4, CH_4, CF_4 ***Mitchell & Boudon****)*

Graphical approach to rotation-vibration-spin Hamiltonian

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

to help understand complex rotational spectra and dynamics.

<u>OUTLINE</u>

	<u>Example(s)</u>
Introductory review	
• *Rovibronic nomograms and PQR structure*	ν_3 and ν_4 SF_6
• *Rotational Energy Surfaces (RES) and θ^J_K-cones*	ν_4 P(88) SF_6
• *Spin symmetry correlation tunneling and entanglement*	SF_6
Recent developments	
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• *Rotational Energy Eigenvalue Surfaces (REES)*	ν_3 SF_6

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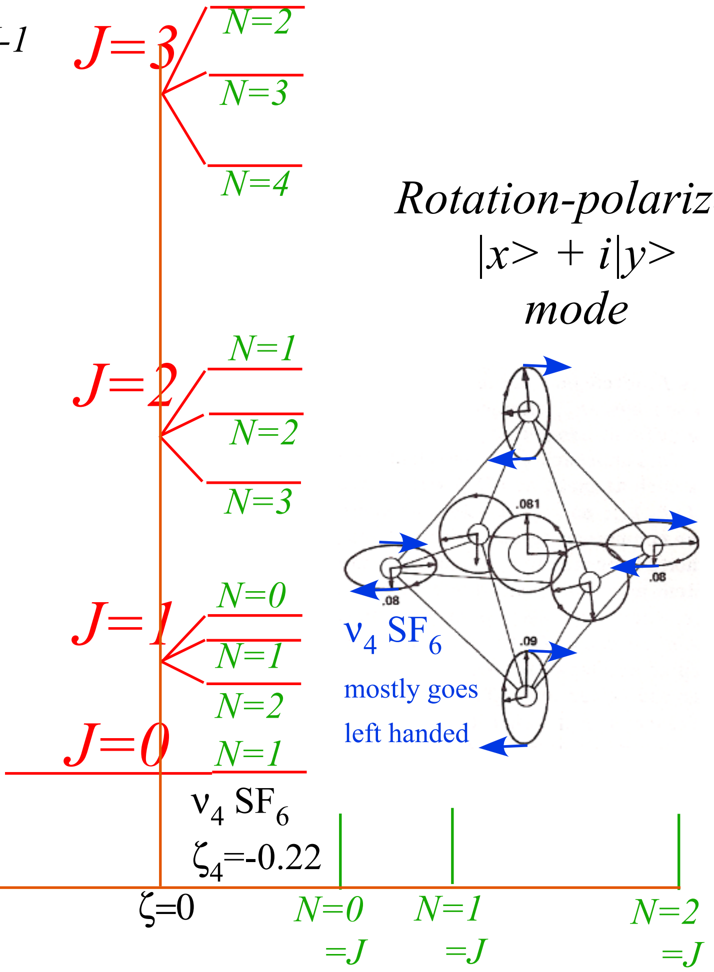
$$\langle H\rangle \sim \nu_{vib}+BN(N+1)+2B(1-\zeta)\cdot\begin{cases} N+1 & \text{for : } J=N+1 \\ 0 & \text{for : } J=N \\ N & \text{for : } J=N-1 \end{cases}$$

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

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



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

ν_4 SF$_6$
mostly goes
left handed

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

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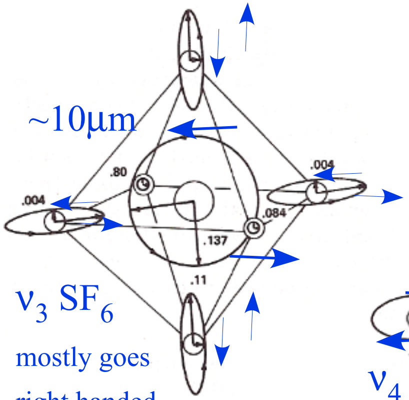
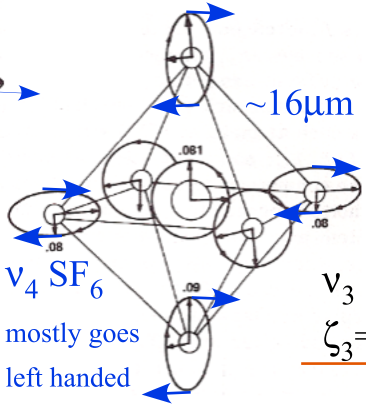


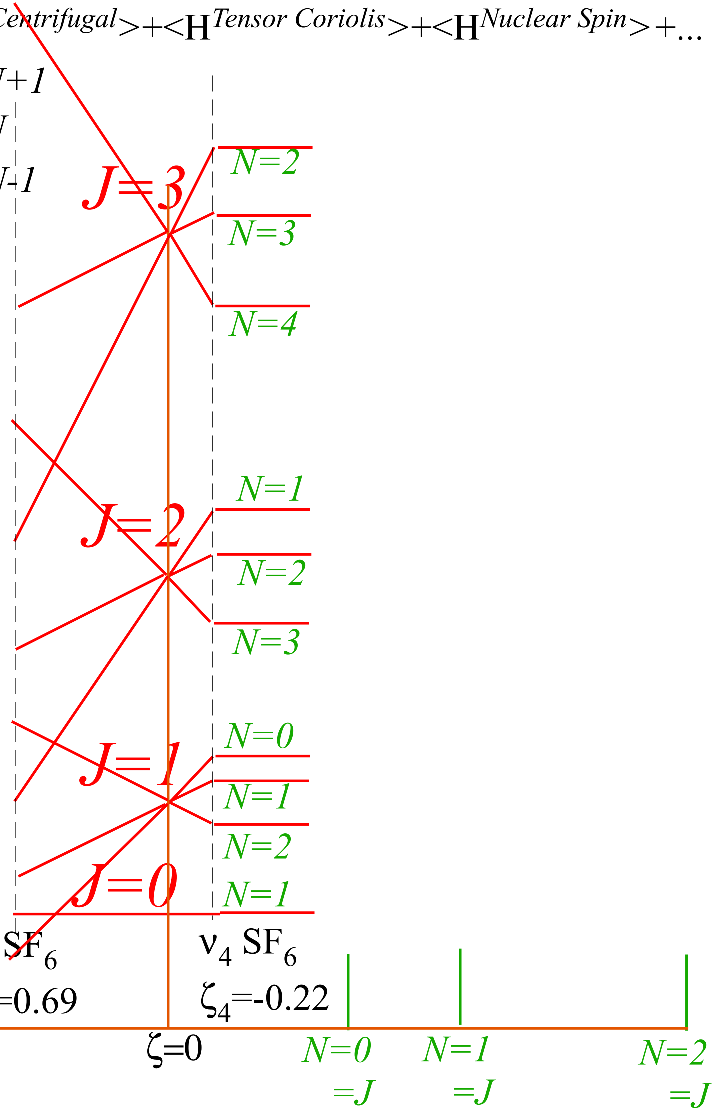
ν$_3$ SF$_6$

mostly goes right handed



ν$_4$ SF$_6$

mostly goes left handed



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

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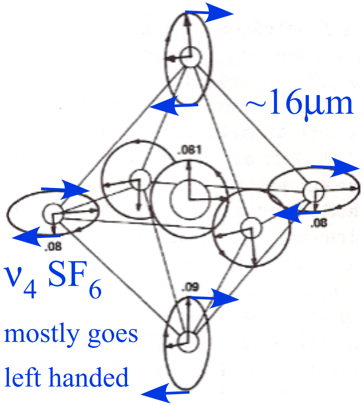
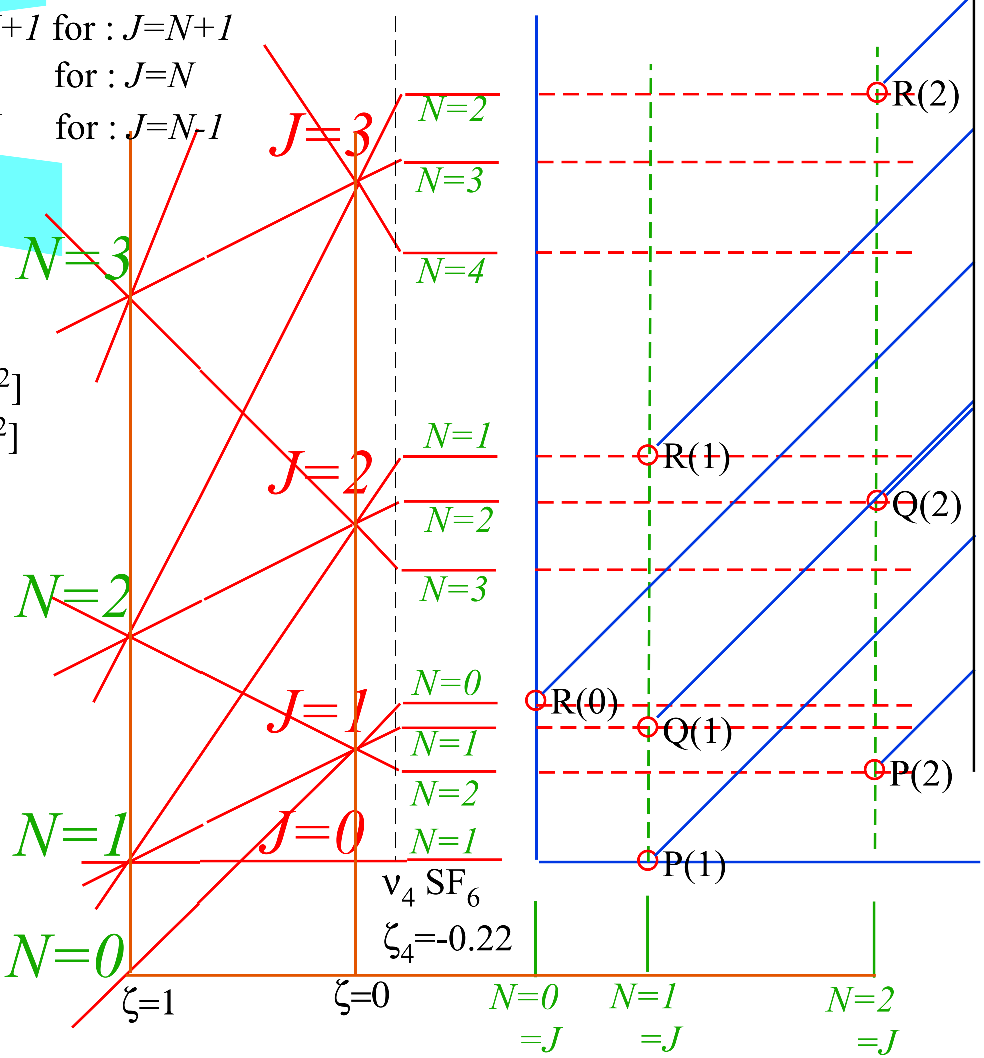


ν_4 SF$_6$

mostly goes

left handed



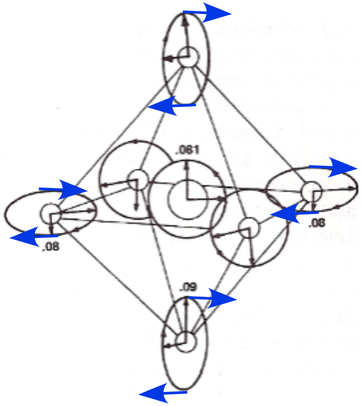
ν_4 SF$_6$

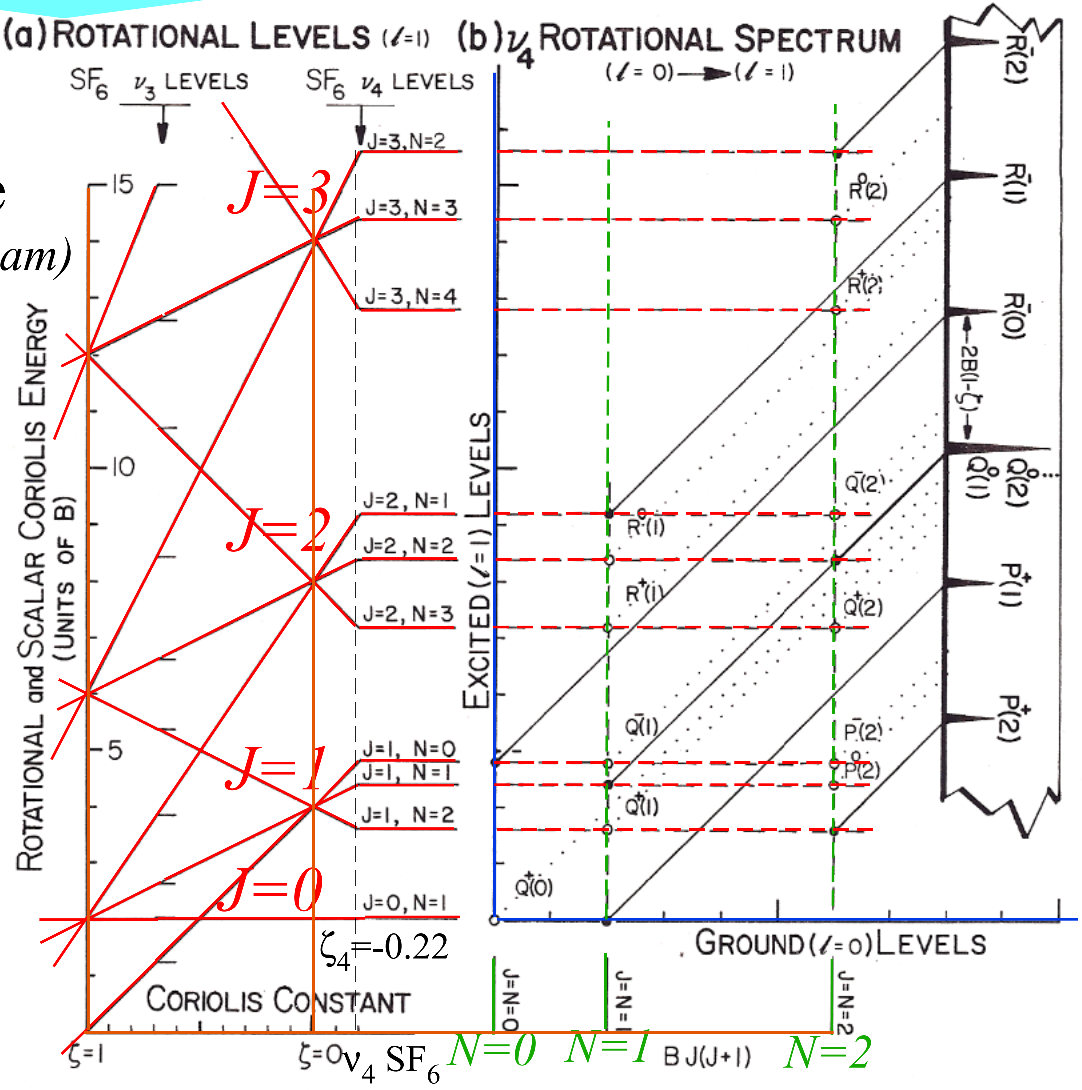
ζ_4=-0.22

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

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

(Using rovib. nomogram)





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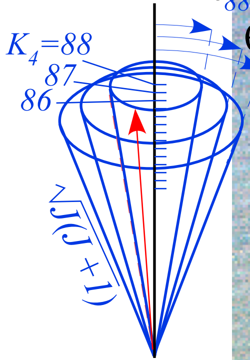
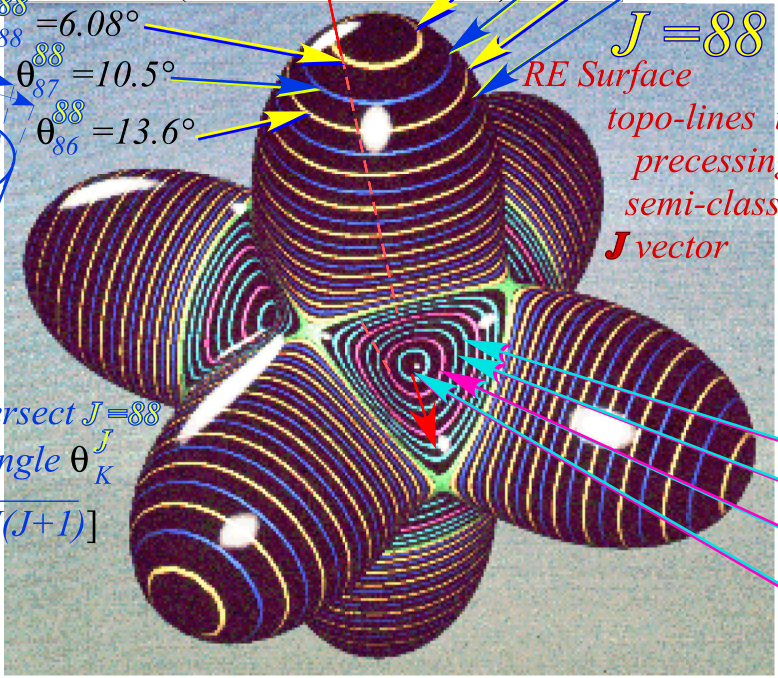
O_h or T_d Spherical Top: *(Hecht CH_4 Hamiltonian 1960)*

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

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

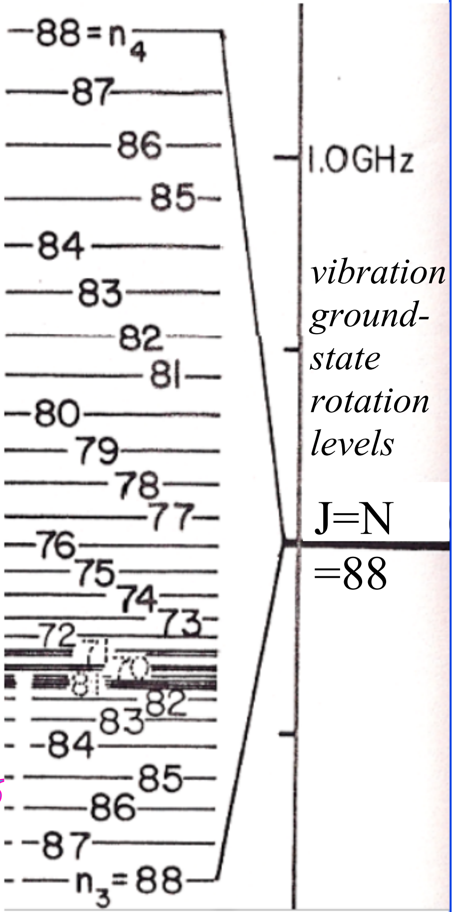




RE Surface topo-lines track precessing semi-classical ***J*** vector

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

θ^J_K= acos$[K/\sqrt{J(J+1)}]$



vibration ground-state rotation levels

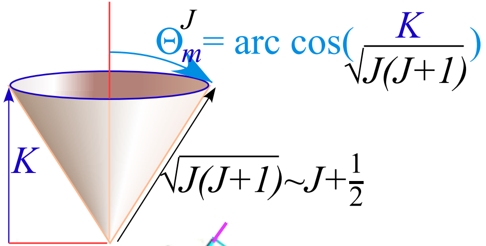
(next page shows slice)

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

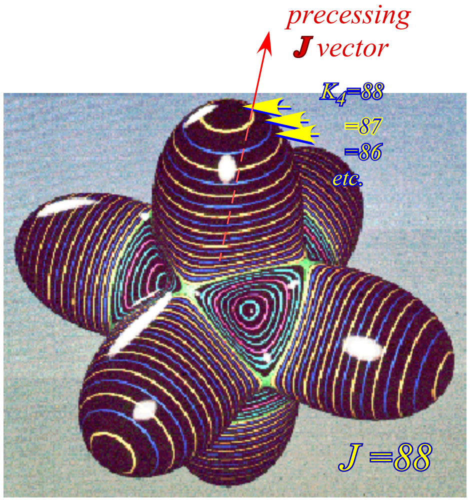
and J-cone intersection

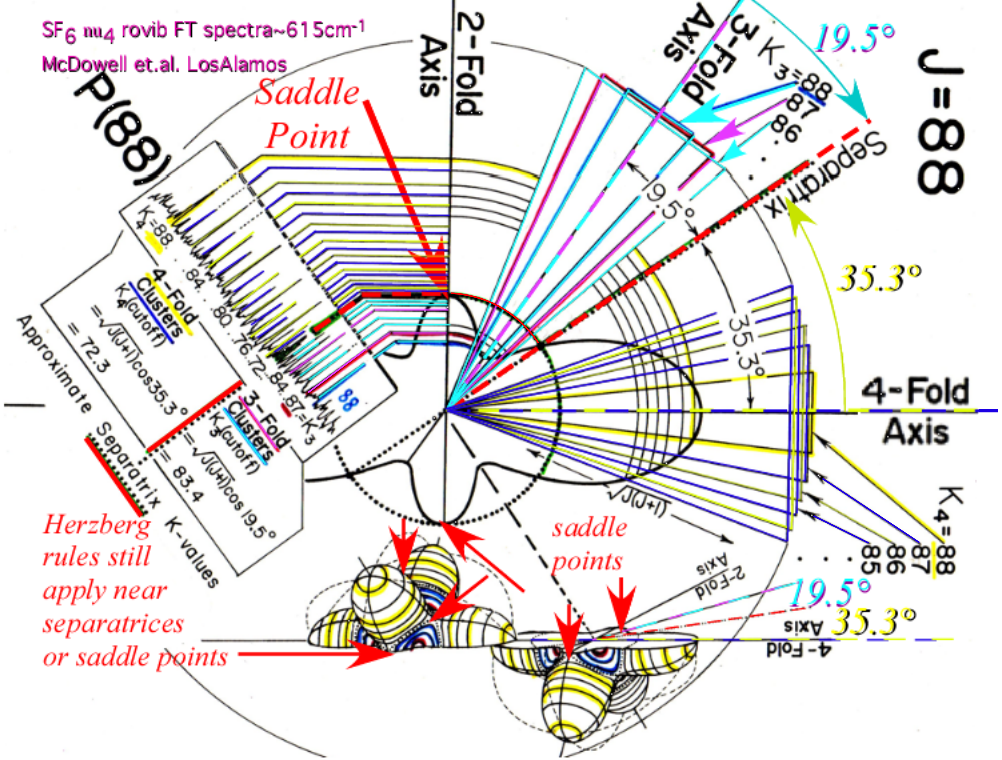
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

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

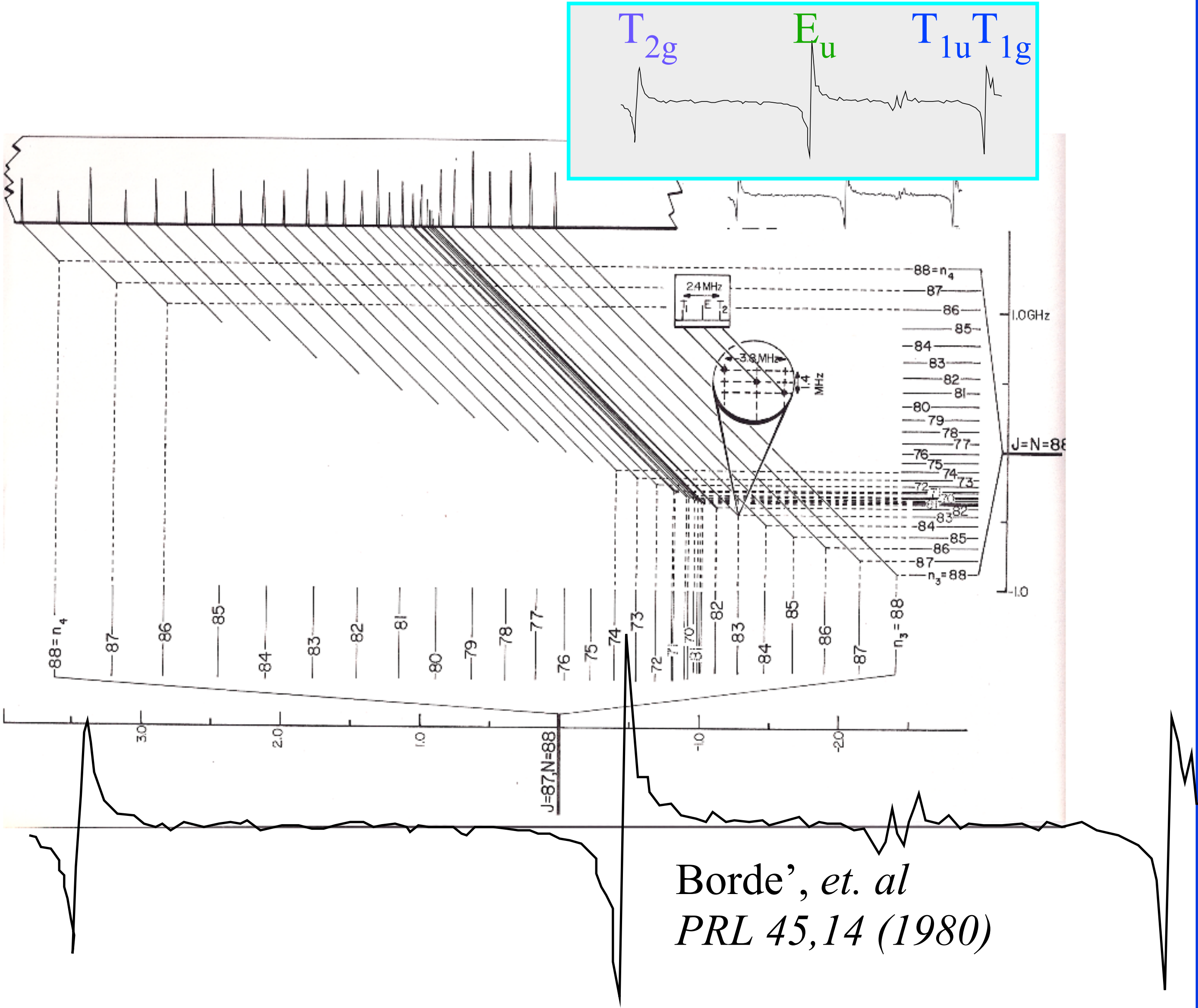


Rovibronic Energy (RE) Tensor Surface





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



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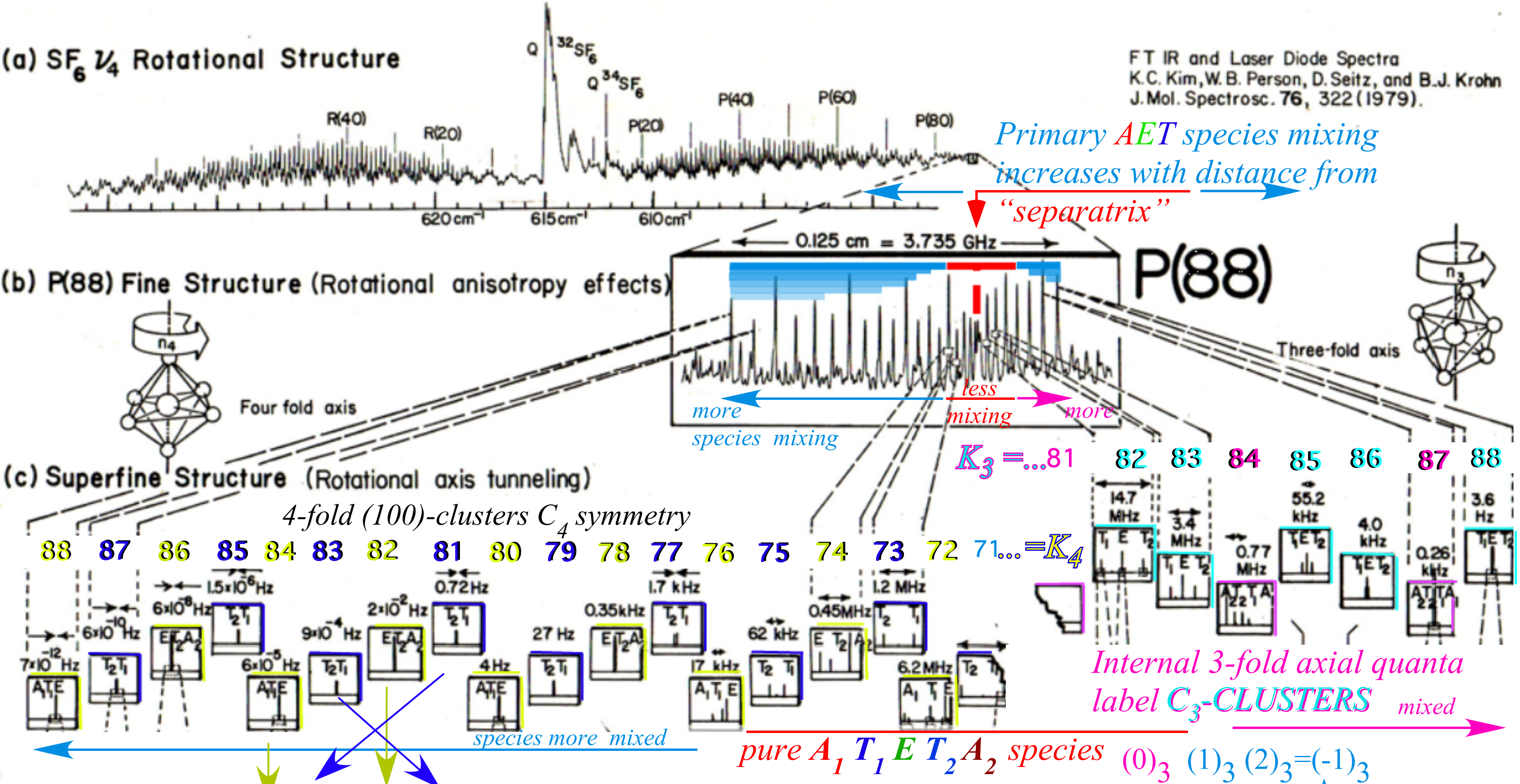


Primary AET species mixing increases with distance from "separatrix"

Internal 3-fold axial quanta label C_3-CLUSTERS

pure A_1 T_1 E T_2 A_2 species

Cubic Octahedral symmetry O

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

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

83=84-1

4-fold (1oo) C_4 symmetry clusters

3-fold (111) C_3 symmetry clusters

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

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

86=88-1

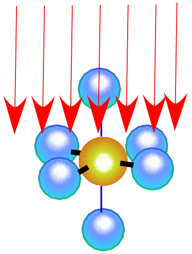
Duality: The "Flip Side" of Symmetry Analysis.

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

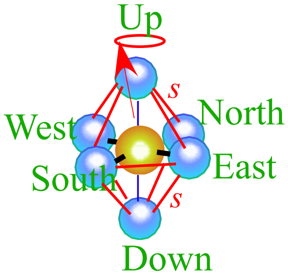


Example:
Cubic-Octahedral O
reduced to
Tetragonal C_4

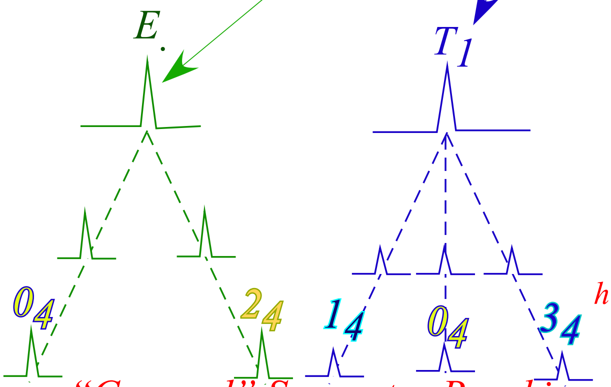
C_4	0_4	1_4	2_4	3_4
A_1	1	.	.	.
A_2	.	.	1	.
E	1.	.	1	.
T_1	1	1	.	1
T_2	.	1	1	1

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



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

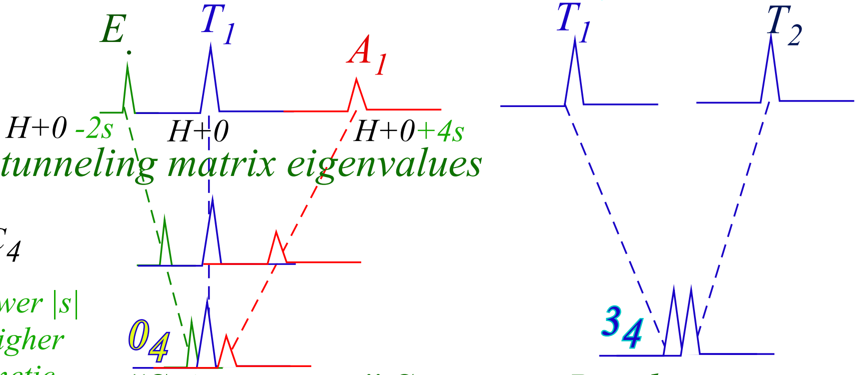


"Coerced" Symmetry Breaking

Stronger C_4

*higher |**B**|*

lower |s|
(higher
kinetic
barriers)



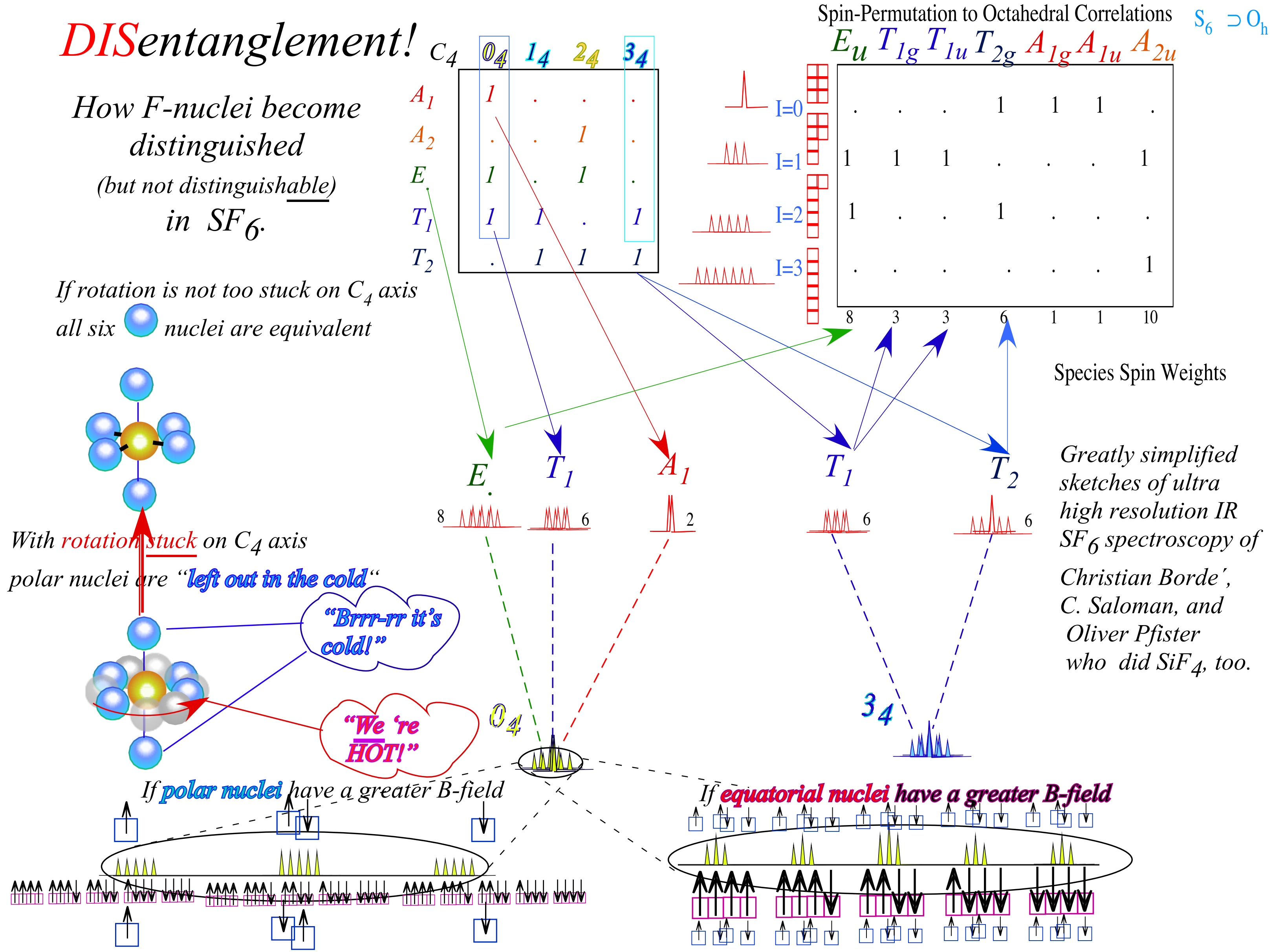
"Spontaneous" Symmetry Breaking

DISentanglement!

How F-nuclei become distinguished

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

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

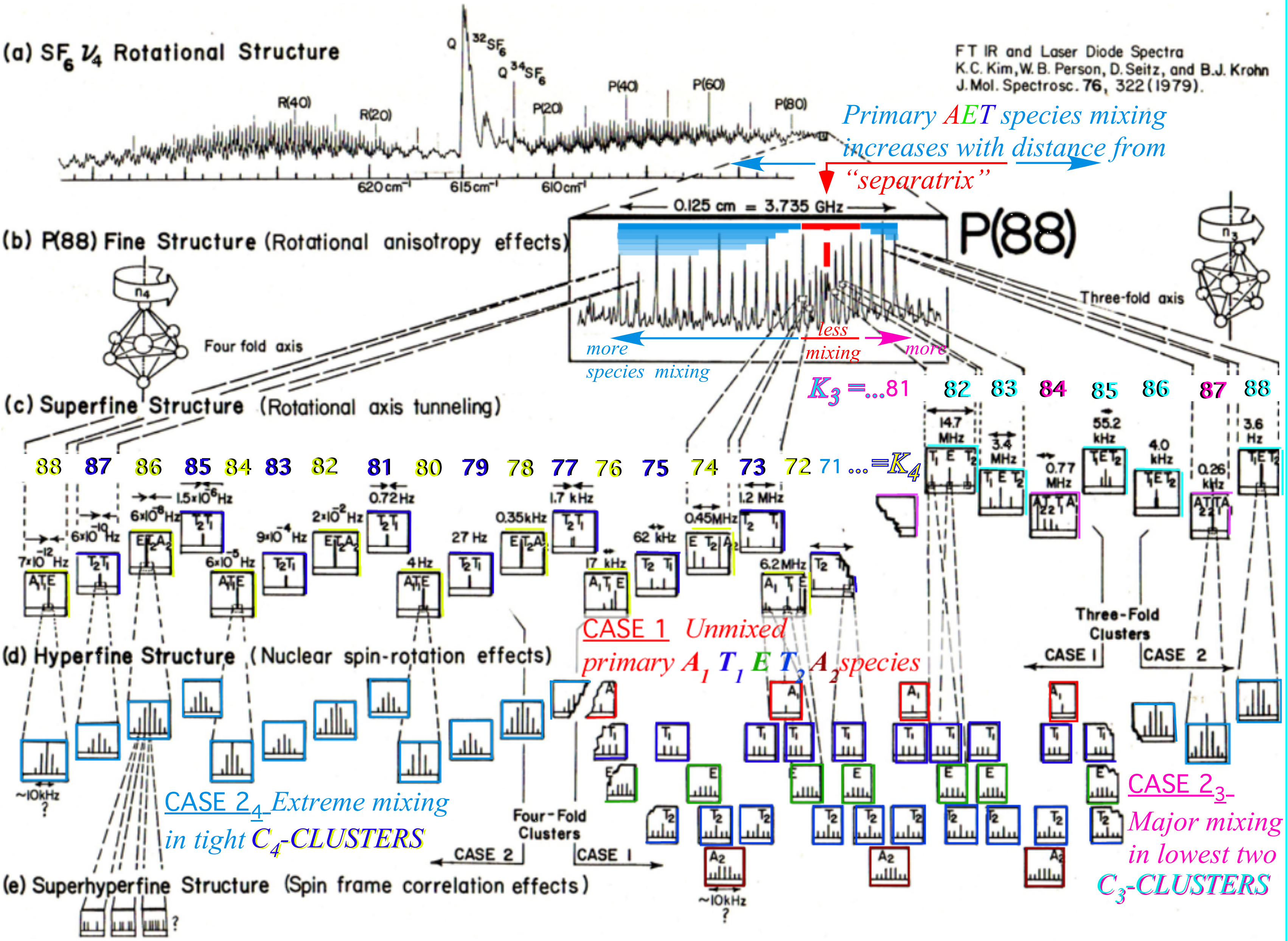
If rotation is not too stuck on C_4 axis all six nuclei are equivalent

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

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

*If **polar nuclei** have a greater B-field*

*If **equatorial nuclei have a greater B-field***



Primary AET species mixing increases with distance from "separatrix"

more species mixing

less mixing

more

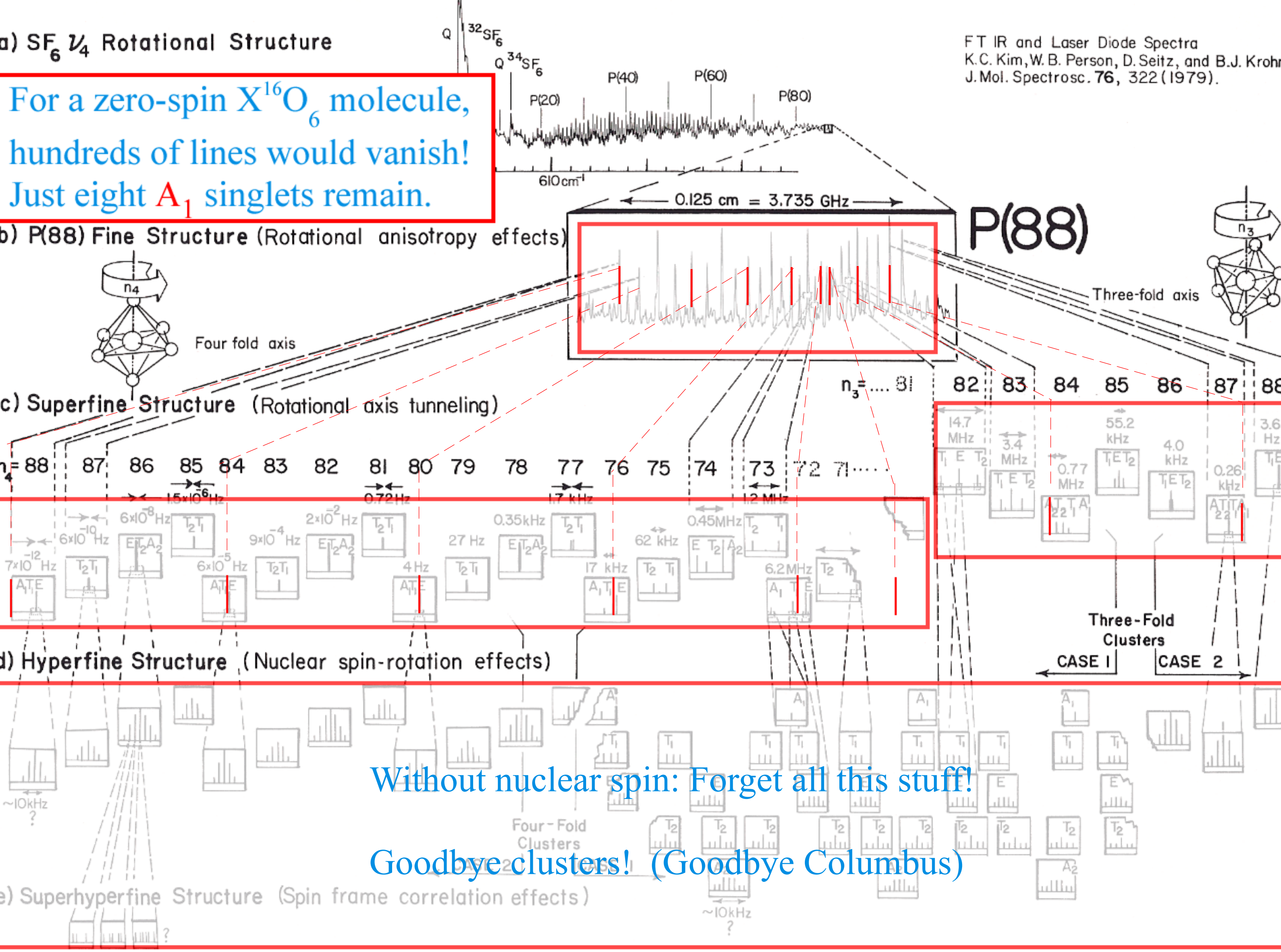
K_3 =...81 82 83 84 85 86 87 88

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*

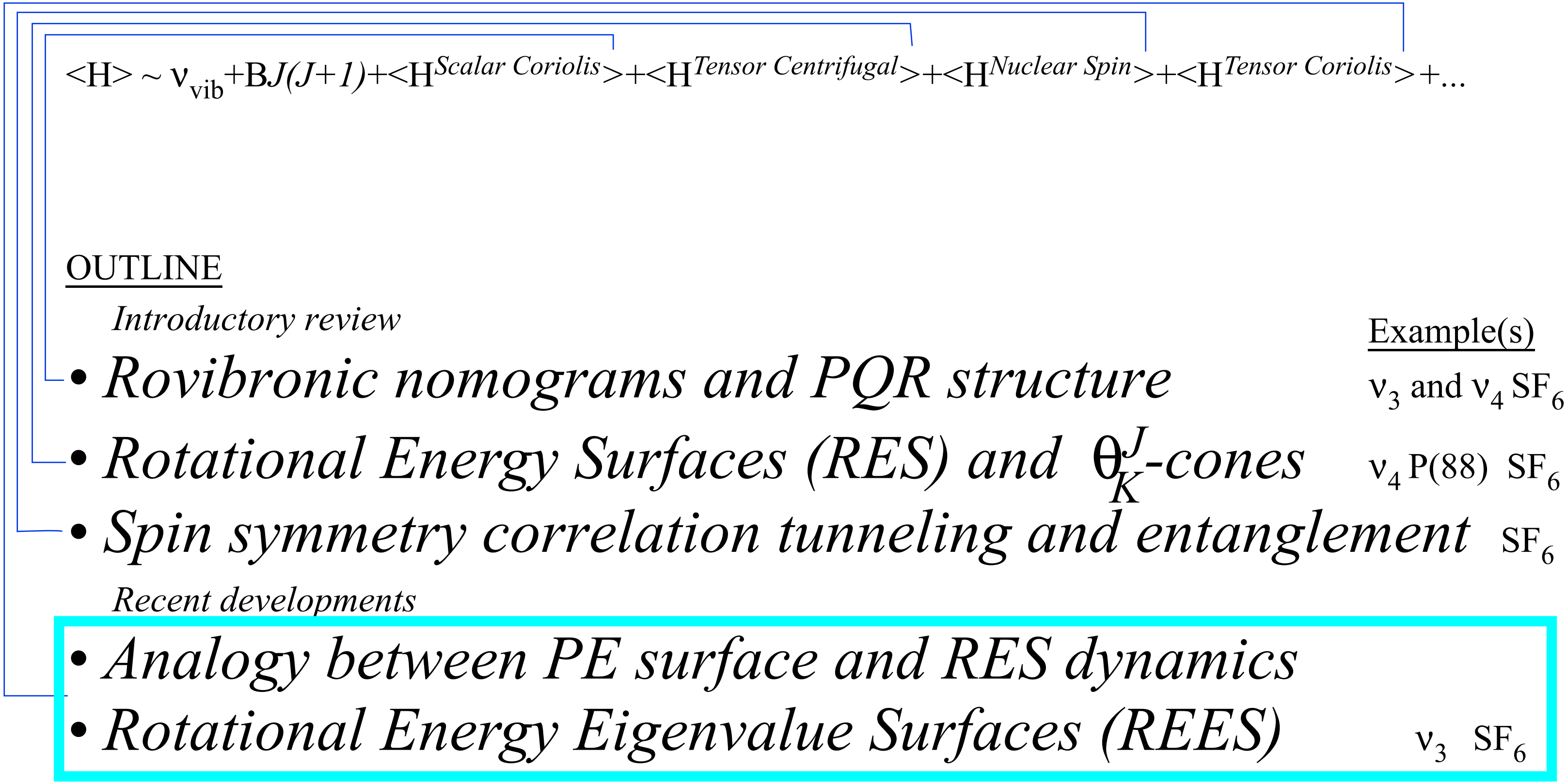


For a zero-spin $X^{16}O_6$ molecule, hundreds of lines would vanish! Just eight A_1 singlets remain.

Without nuclear spin: Forget all this stuff!

Goodbye clusters! (Goodbye Columbus)

Graphical approach to rotation-vibration-spin Hamiltonian



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

OUTLINE

Introductory review

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

Recent developments

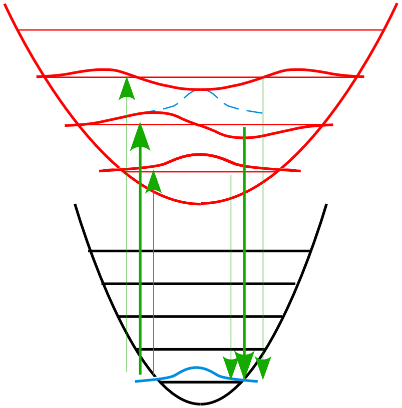
• *Analogy between PE surface and RES dynamics*	
• *Rotational Energy Eigenvalue Surfaces (REES)*	ν_3 SF_6

Potenial Energy Surface (PES) Dynamics

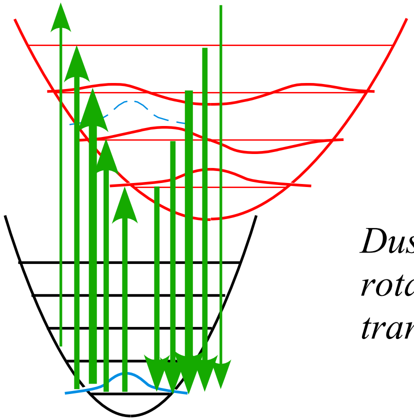
Inter-PES electronic transitions

Vibrational Franck-Condon effects

- Frequency mismatch of PES



- Shape or position mismatch of PES



Duschinsky rotation or translation

Analogy between

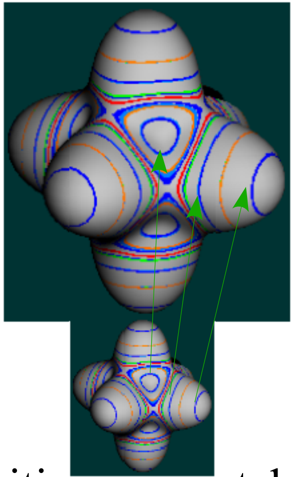
Vibronic and Rovibronic

Rotation Energy Surface (RES) Dynamics

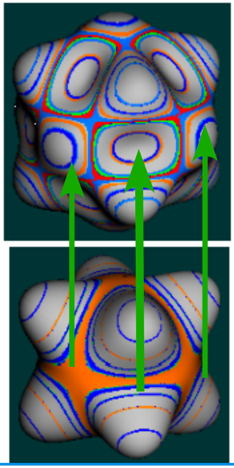
Inter-PES electronic transitions

Rotational "Franck-Condon" effects

- Frequency mismatch of RES



- Shape or position mismatch of RES



Non-Born-Oppenheimer Surfaces

Strong vibration-electronic mixing

Jahn-Teller-Renner effects

- Multiple and variable conformer minima

Rotation Energy Eigen-Surfaces (REES)

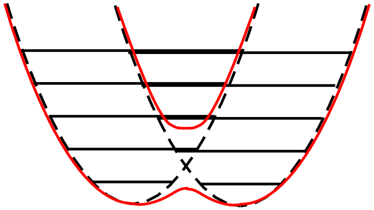
Inter-PES electronic transitions

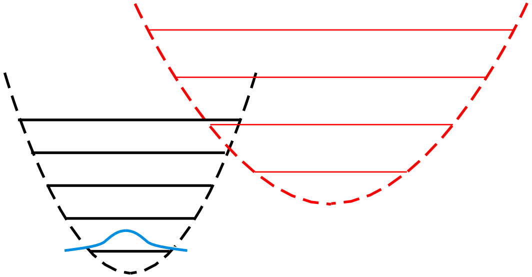
Rotational JTR effects

- Multiple and variable J-axes

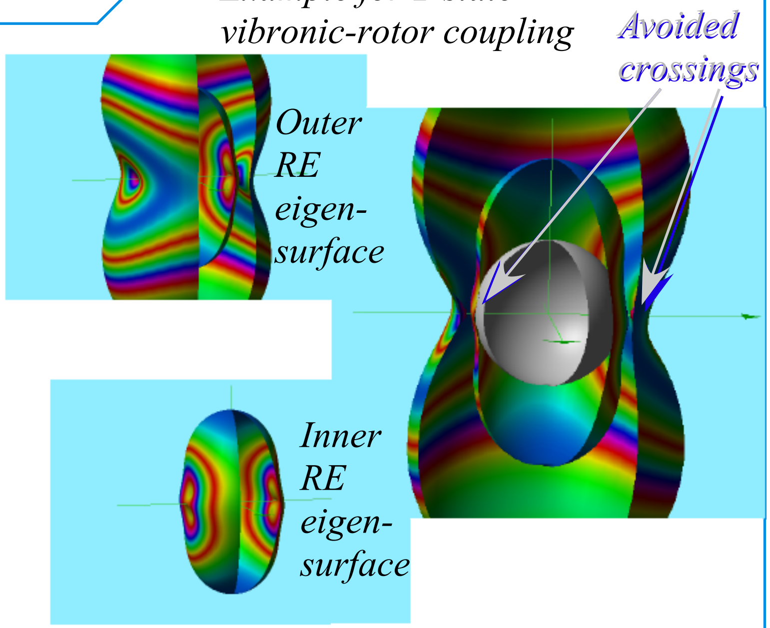
Analogy between

Vibronic and Rovibronic





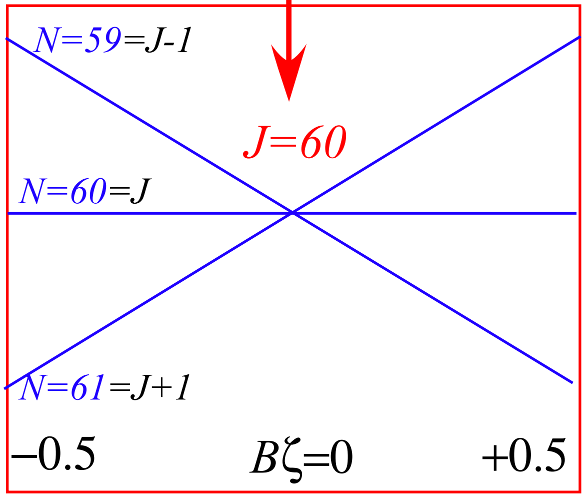
Example for 2-state vibronic-rotor coupling

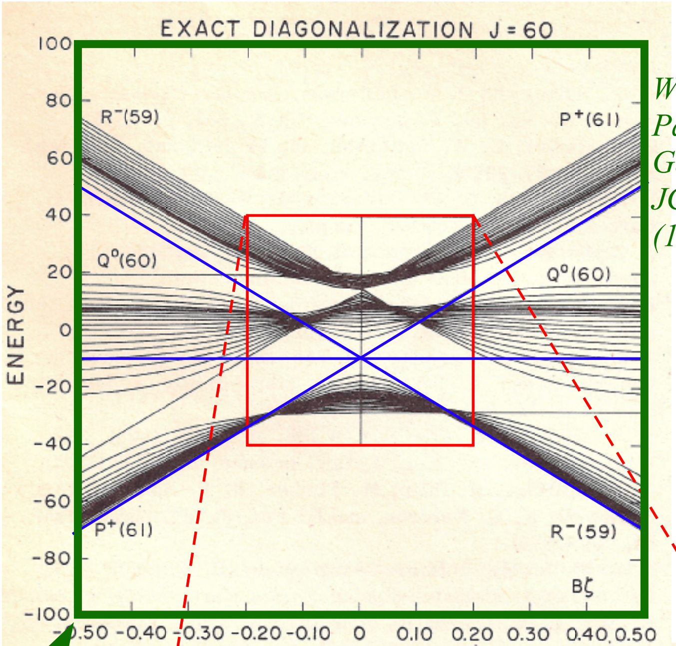


Recall scalar Coriolis

PQR plots vs. $B\zeta$

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



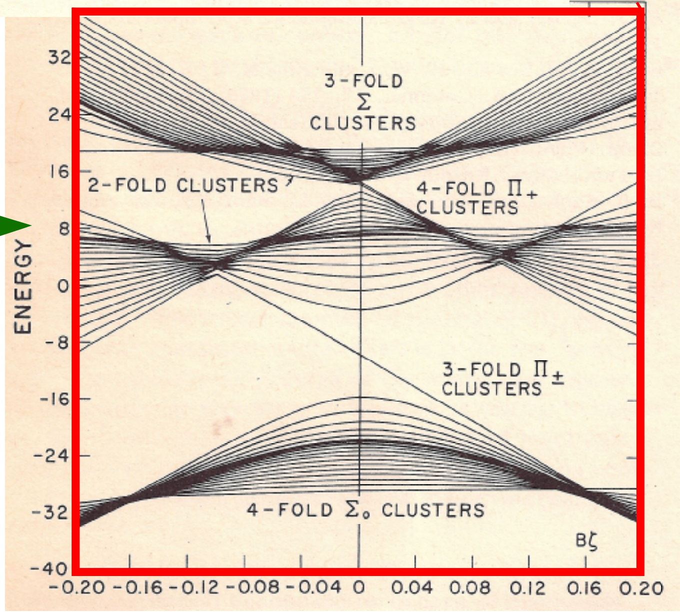


WGH, Patterson, Galbraith JCP 69, 4906 (1978)

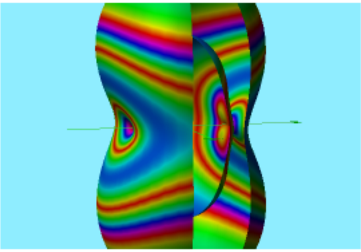
Now consider this plot with *tensor* Coriolis, too

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

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



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



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

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

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

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

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

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

Body-ΣΠ±-Basis

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

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

Lab-PQR-Basis

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

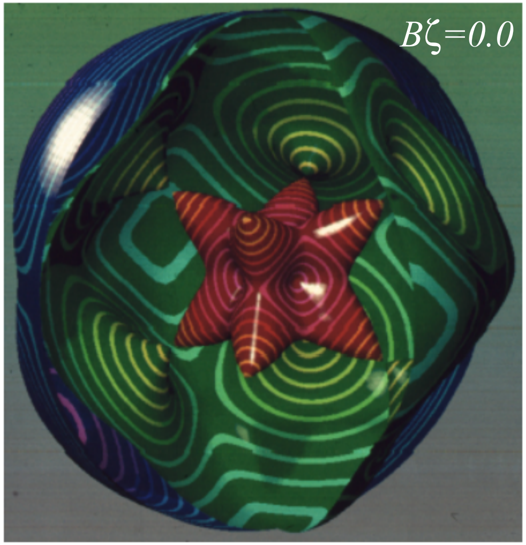
(Either basis should give same REES)

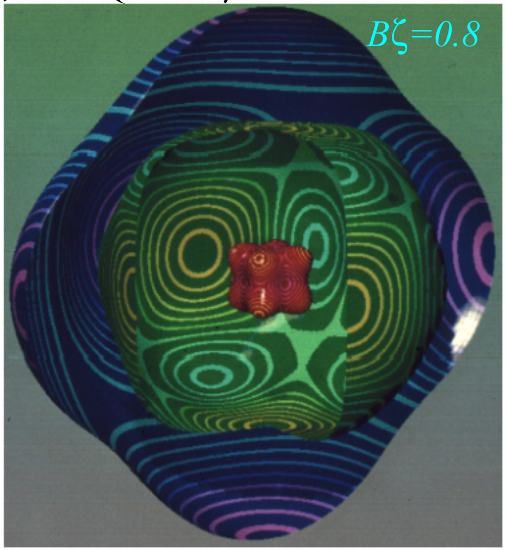
$$+2t_{224}|J|^2\begin{pmatrix}H_{PP} & H_{PQ} & H_{PR}\\ H^*_{PQ} & H_{QQ} & H_{QR}\\ H^*_{RP} & H^*_{QR} & H_{RR}\end{pmatrix}$$

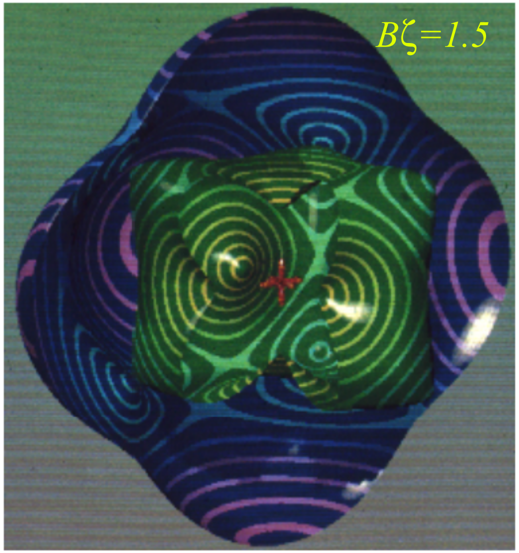
$$H_{PP}=(35\cos^4\beta-30\cos^2\beta+5\sin^2\beta\sin4\gamma+5)/4=H_{RR}$$

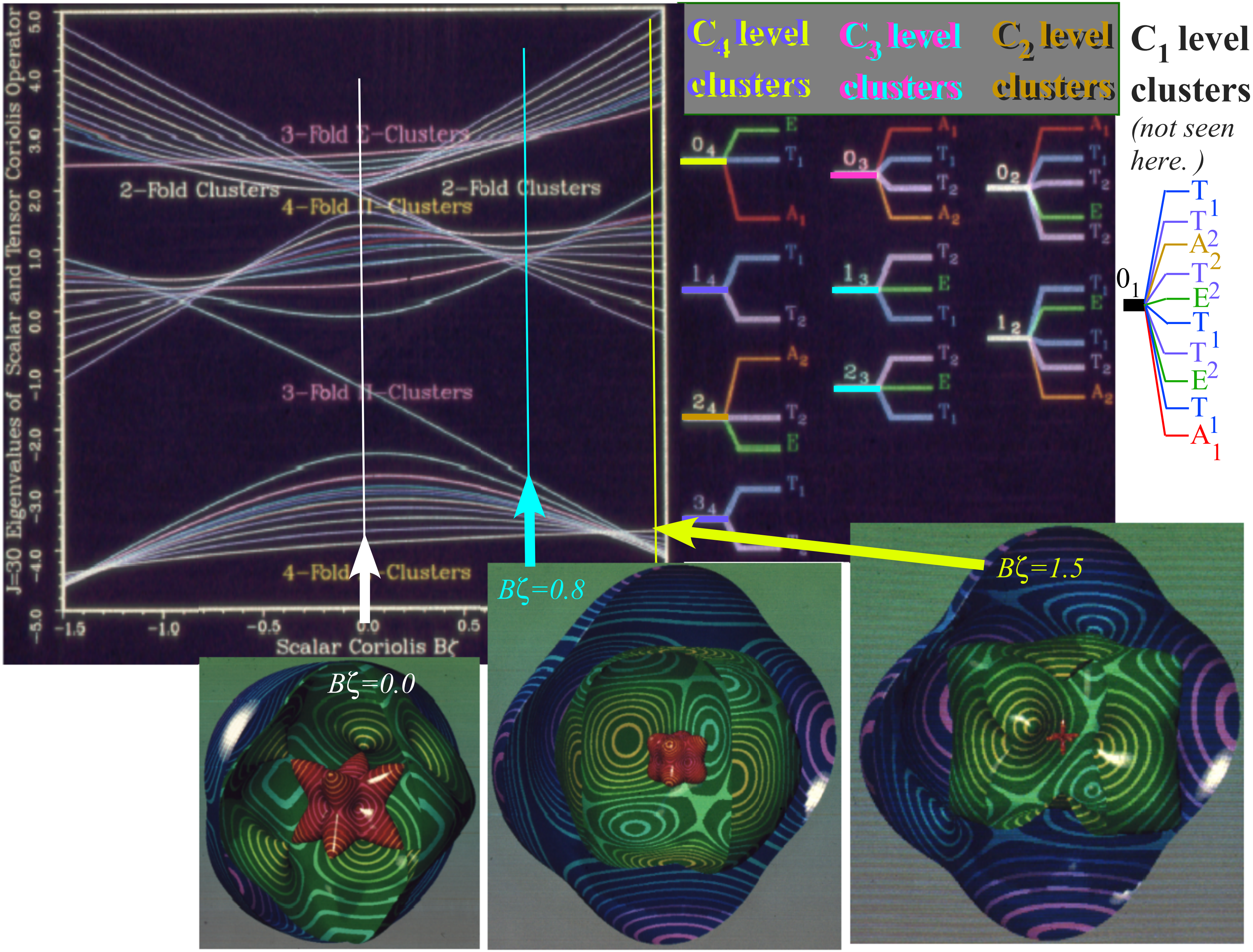
$$H_{PQ}=5\sin\beta(7\cos^2\beta-3\cos\beta-\sin^2\beta(\cos\beta\cos4\gamma+i\sin4\gamma))/\sqrt{8}=H_{QR}$$

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









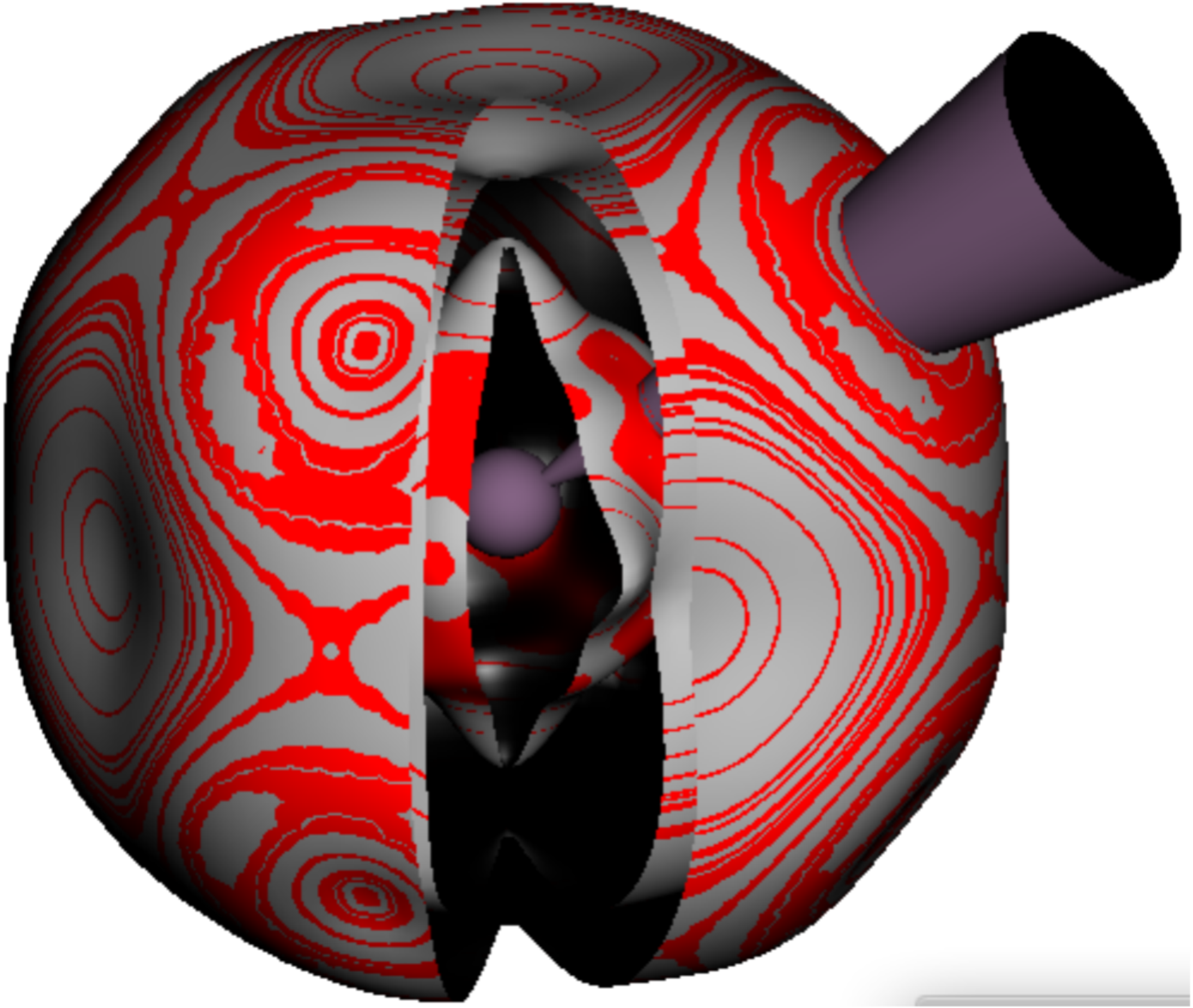
C_4 level clusters

C_3 level clusters

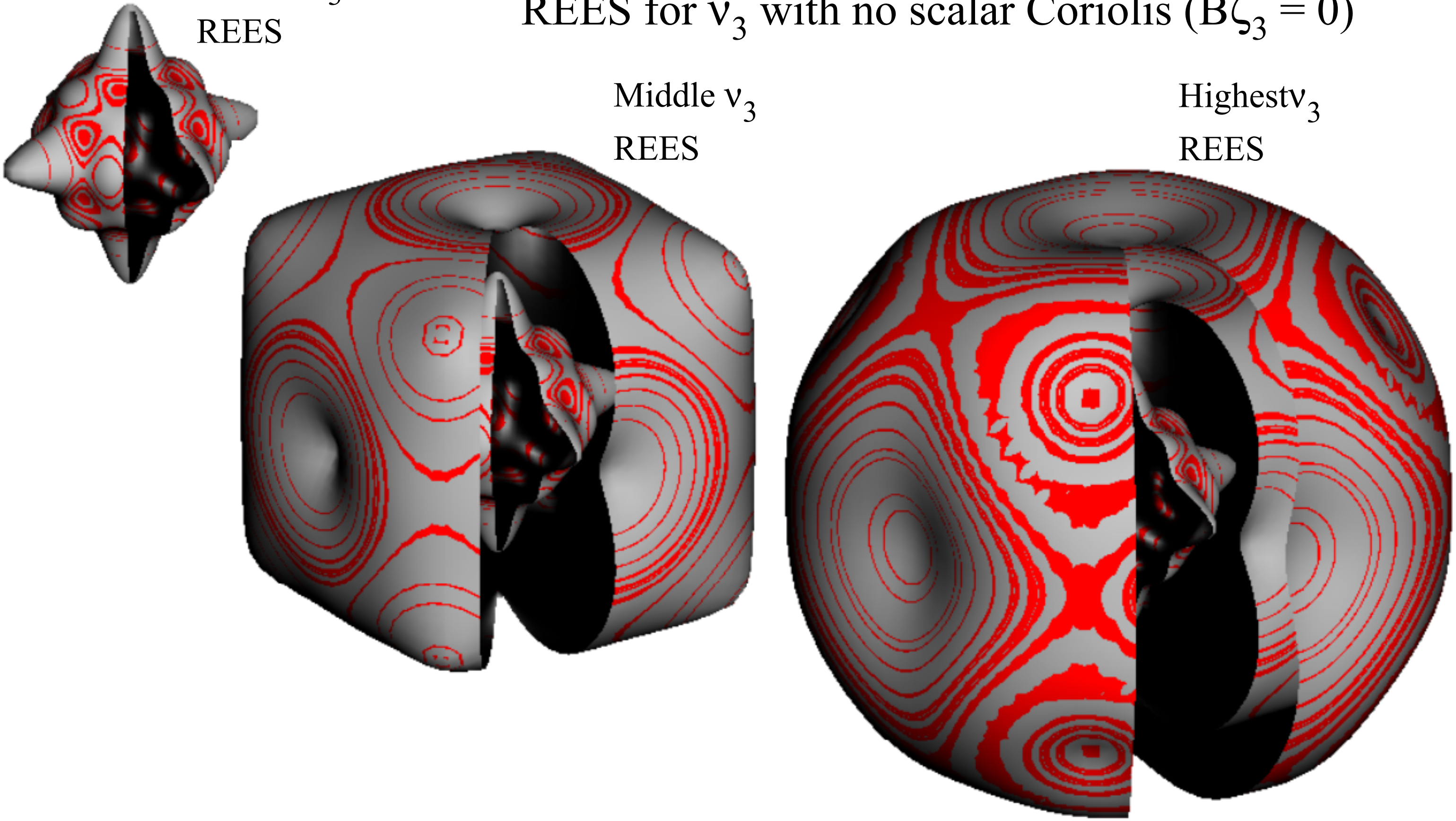
C_2 level clusters

C_1 level clusters

(not seen here.)



REES for ν_3 with no scalar Coriolis ($B\zeta_3 = 0$)



Lowest ν_3
REES

Middle ν_3
REES

Highestν_3
REES

Summary

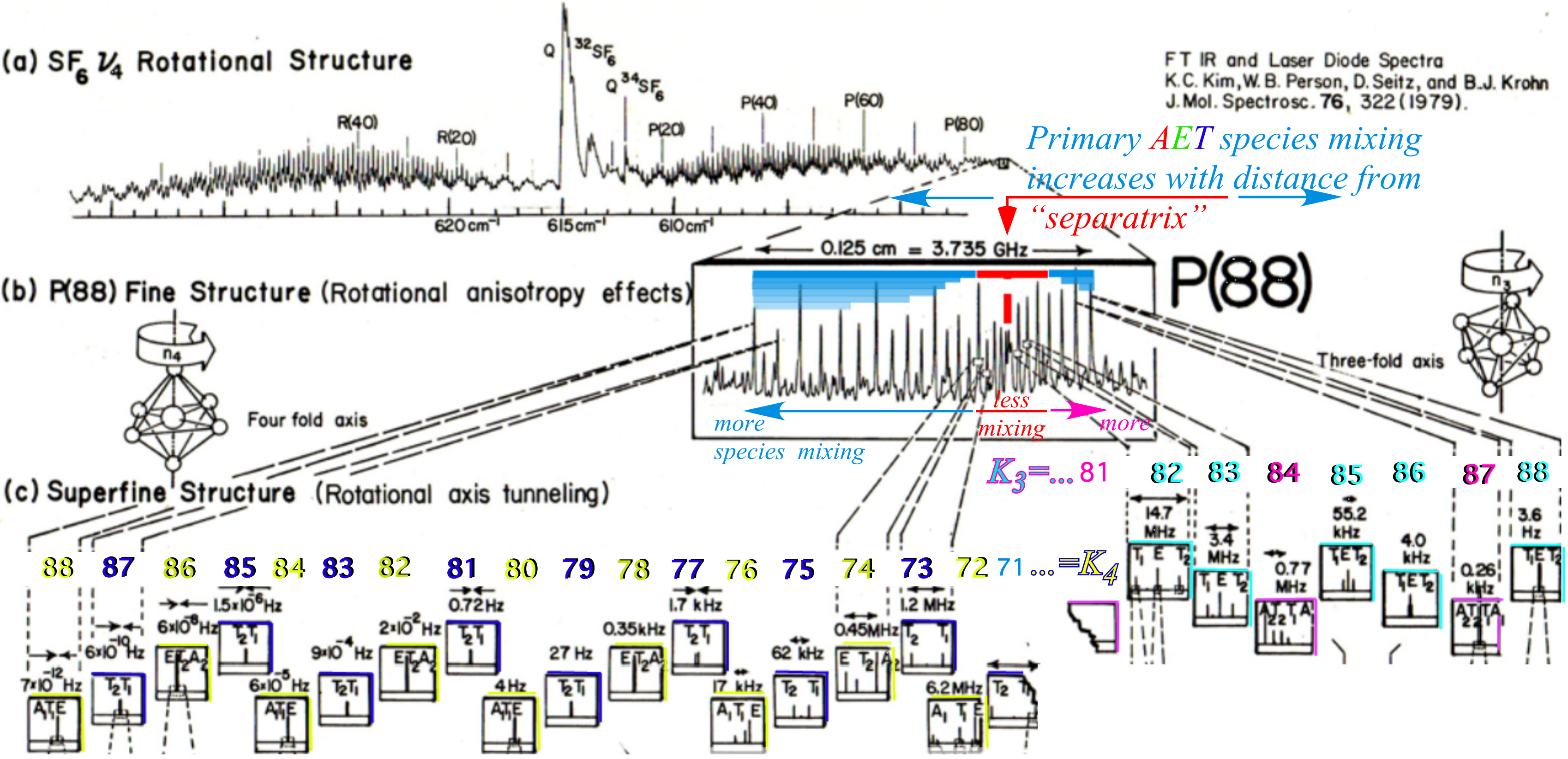
- *Spin symmetry, orientation, rotation, and permuation are underlying properties that molecules have before any excitation begins. Ignore them and you may miss some cool stuff!*

- *Graphical techniques help to expose symmetry properties. We discussed*
  - *rovibronic nomograms*
  - *rotational energy surfaces (RES)*
  - *rotation energy eigenvalue surfaces (REES)*
  - *effects that entangle and disentangle spin states*

- *REES effects have useful analogy with vibronic effects.*

- *Spin symmetry species are are quite mutable.*

Perhaps, they may be optically controlled.



Primary AET species mixing increases with distance from "separatrix"

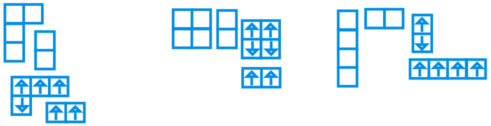
more species mixing

less mixing

more

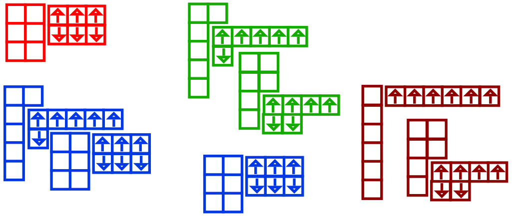
CASE 2_4

Broken 4 + 2 tableau state description



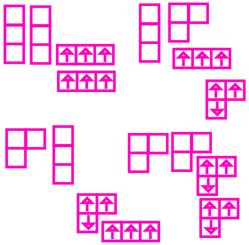
Spin-rovib ENTANGLEMENT symmetry might be controllable!

CASE 1 *Unmixed primary A_1 T_1 E T_2 A_2 species (Whole 6-box tableaus)*

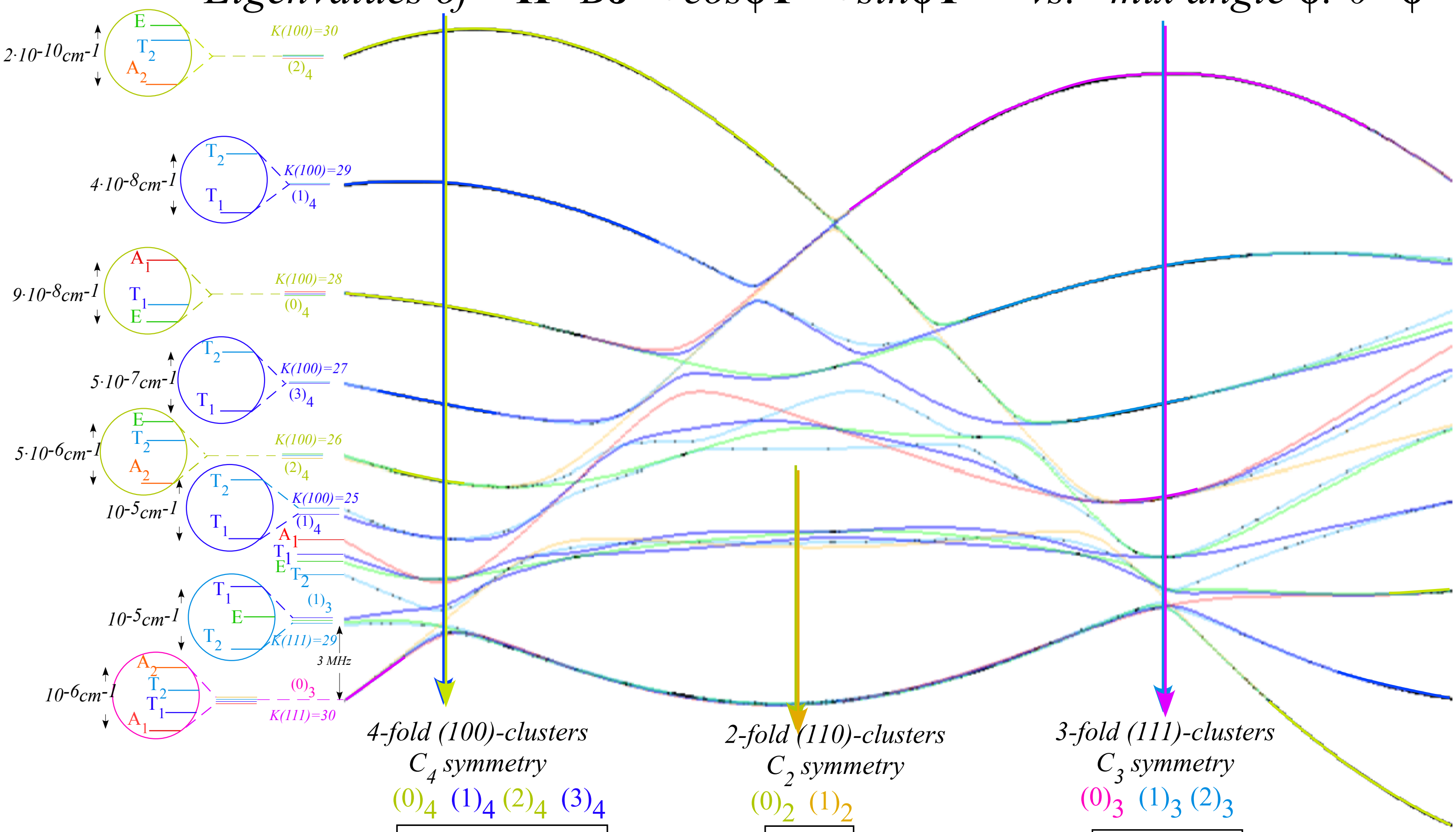


CASE 2_3

Broken 3 + 3 Tableaus



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



4-fold (100)-clusters
C_4 symmetry

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

2-fold (110)-clusters
C_2 symmetry

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

Cubic
Octahedral
symmetry
O

3-fold (111)-clusters
C_3 symmetry

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

(not
present)
no-symmetry
clusters

	C_1 $(0)_1$
A_1	1
A_2	1
E_2	2
T_1	3
T_2	3

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