4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Molecular rovibrational spectra : O_h symmetry, SF_6 and UF_6 examples

SF_6 has octahedral ($O_h \supset O \supset C_{4v}$ or C_{3v}) symmetry
SF_6 octahedral ($O_h \supset C_{4v}$) Cartesian coordination
SF_6 octahedral ($O_h \supset C_{4v}$) symmetry coordination
  SF_6 octahedral ($O_h \supset C_{4v}$) mode labeling
Ireps for $O \supset D_4 \supset D_2$ subgroup chain and coset factored projectors
  Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors
  Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum
Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics
  Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics
  Modes and energy level diagrams: SF_6, UF_6, etc.
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Tensor centrifugal and Coriolis T_{1u} effects in ν_4 P(88) fine structure
  Nomogram of T_{1u} SF_6 ν_4 P(88) fine, superfine, and hyperfine structure

AMOP reference links *(Updated list given on **2nd** and 3rd pages of each class presentation)*

Web Resources - front page
UAF Physics UTube channel

Quantum Theory for the Computer Age
Principles of Symmetry, Dynamics, and Spectroscopy
Classical Mechanics with a Bang!
Modern Physics and its Classical Foundations

2014 AMOP
2017 Group Theory for QM
2018 AMOP

Representaions Of Multidimensional Symmetries In Networks - harter-jmp-1973

Alternative Basis for the Theory of Complex Spectra

- Alternative_Basis_for_the_Theory_of_Complex_Spectra_I_-_harter-pra-1973
- Alternative_Basis_for_the_Theory_of_Complex_Spectra_II_-_harter-patterson-pra-1976
- Alternative_Basis_for_the_Theory_of_Complex_Spectra_III_-_patterson-harter-pra-1977

Frame Transformation Relations And Multipole Transitions In Symmetric Polyatomic Molecules - RMP-1978
Asymptotic eigensolutions of fourth and sixth rank octahedral tensor operators - Harter-Patterson-JMP-1979
Rotational energy surfaces and high- J eigenvalue structure of polyatomic molecules - Harter - Patterson - 1984
Galloping waves and their relativistic properties - ajp-1985-Harter
Rovibrational Spectral Fine Structure Of Icosahedral Molecules - Cpl 1986 (Alt Scan)

Theory of hyperfine and superfine levels in symmetric polyatomic molecules.

I) Trigonal and tetrahedral molecules: Elementary spin-1/2 cases in vibronic ground states - PRA-1979-Harter-Patterson (Alt scan)
II) Elementary cases in octahedral hexafluoride molecules - Harter-PRA-1981 (Alt scan)

Rotation–vibration spectra of icosahedral molecules.

I) Icosahedral symmetry analysis and fine structure - harter-weeks-jcp-1989 (Alt scan)
II) Icosahedral symmetry, vibrational eigenfrequencies, and normal modes of buckminsterfullerene - weeks-harter-jcp-1989 (Alt scan)
III) Half-integral angular momentum - harter-reimer-jcp-1991

Rotation-vibration scalar coupling zeta coefficients and spectroscopic band shapes of buckminsterfullerene - Weeks-Harter-CPL-1991 (Alt scan)
Nuclear spin weights and gas phase spectral structure of 12C60 and 13C60 buckminsterfullerene -Harter-Reimer-Cpl-1992 - (Alt1, Alt2 Erratum)
Gas Phase Level Structure of C60 Buckyball and Derivatives Exhibiting Broken Icosahedral Symmetry - reimer-diss-1996
Fullerene symmetry reduction and rotational level fine structure/ the Buckyball isotopomer 12C 13C59 - jcp-Reimer-Harter-1997 (HiRez)
Wave Node Dynamics and Revival Symmetry in Quantum Rotors - harter - jms - 2001
Molecular Symmetry and Dynamics - Ch32-Springer Handbooks of Atomic, Molecular, and Optical Physics - Harter-2006

Resonance and Revivals

I) QUANTUM ROTOR AND INFINITE-WELL DYNAMICS - ISMSLi2012 (Talk) OSU knowledge Bank
II) Comparing Half-integer Spin and Integer Spin - Alva-ISMS-Ohio2013-R777 (Talks)
III) Quantum Resonant Beats and Revivals in the Morse Oscillators and Rotors - (2013-Li-Diss)

Resonance and Revivals in Quantum Rotors - Comparing Half-integer Spin and Integer Spin - Alva-ISMS-Ohio2013-R777 (Talk)
Molecular Eigensolution Symmetry Analysis and Fine Structure - IJMS-harter-mitchell-2013
Quantum Revivals of Morse Oscillators and Farey-Ford Geometry - Li-Harter-cpl-2013
QTCA Unit 10 Ch 30 - 2013
AMOP Ch 0 Space-Time Symmetry - 2019

**In development - a web based A.M.O.P. oriented reference page, with thumbnail/previews, greater control over the information display, and eventually full on* Apache-SOLR *Index and search for* nuanced, whole-site content/metadata level *searching.*

AMOP reference links *(Updated list given on 2nd and **3rd** pages of each class presentation)*

(Int.J.Mol.Sci, 14, 714(2013) p.755-774 , *QTCA Unit 7 Ch. 23-26),* *(PSDS - Ch. 5, 7)*

Int.J.Mol.Sci, 14, 714(2013), *QTCA Unit 8 Ch. 23-25,* *QTCA Unit 9 Ch. 26,* *PSDS Ch. 5,* *PSDS Ch. 7*

Intro spin ½ coupling
Unit 8 Ch. 24 p3

H atom hyperfine-B-level crossing
Unit 8 Ch. 24 p15

Hyperf. theory Ch. 24 p48.

Hyperf. theory Ch. 24 p48.
Deeper theory ends p53

Intro 2p3p coupling
Unit 8 Ch. 24 p17.

Intro LS-jj coupling
Unit 8 Ch. 24 p22.

CG coupling derived (start)
Unit 8 Ch. 24 p39.

CG coupling derived (formula)
Unit 8 Ch. 24 p44.

Lande' g-factor
Unit 8 Ch. 24 p26.

Irrep Tensor building
Unit 8 Ch. 25 p5.

Irrep Tensor Tables
Unit 8 Ch. 25 p12.

Wigner-Eckart tensor Theorem.
Unit 8 Ch. 25 p17.

Tensors Applied to d,f-levels.
Unit 8 Ch. 25 p21.

Tensors Applied to high J levels.
Unit 8 Ch. 25 p63.

Intro 3-particle coupling.
Unit 8 Ch. 25 p28.

Intro 3,4-particle Young Tabl
GrpThLect29 p42.

Young Tableau Magic Formu
GrpThLect29 p46-48.

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AMOP reference links *(Updated list given on 2nd and* ***3rd*** *and* ***4th*** *pages of each class presentation)*

Predrag Cvitanovic's: Birdtrack Notation, Calculations, and Simplification

Chaos_Classical_and_Quantum_-_2018-Cvitanovic-ChaosBook
Group Theory - PUP_Lucy_Day_-_Diagrammatic_notation_-_Ch4
Simplification_Rules_for_Birdtrack_Operators_-_Alcock-Zeilinger-Weigert-zeilinger-jmp-2017
Group Theory - Birdtracks_Lies_and_Exceptional_Groups_-_Cvitanovic-2011
Simplification_rules_for_birdtrack_operators-_jmp-alcock-zeilinger-2017
Birdtracks for SU(N) - 2017-Keppeler

Frank Rioux's: UMA method of vibrational induction

Quantum_Mechanics_Group_Theory_and_C60_-_Frank_Rioux_-_Department_of_Chemistry_Saint_Johns_U
Symmetry_Analysis_for_H20-_H20GrpTheory-_Rioux
Quantum_Mechanics-Group_Theory_and_C60_-_JChemEd-Rioux-1994
Group_Theory_Problems-_Rioux-_SymmetryProblemsX
Comment_on_the_Vibrational_Analysis_for_C60_and_Other_Fullerenes_Rioux-RSP

Supplemental AMOP Techniques & Experiment

Many Correlation Tables are Molien Sequences - Klee (Draft 2016)
High-resolution_spectroscopy_and_global_analysis_of_CF4_rovibrational_bands_to_model_its_atmospheric_absorption-_carlos-Boudon-jqsrt-2017
Symmetry and Chirality - Continuous_Measures_-_Avnir
*

Special Topics & Colloquial References

r-process_nucleosynthesis_from_matter_ejected_in_binary_neutron_star_mergers-PhysRevD-Bovard-2017

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AMOP reference links on pages 2-4

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Intro-O-symmetry Lect.11 p.28.

O-groupTable Lect.11 p.35.

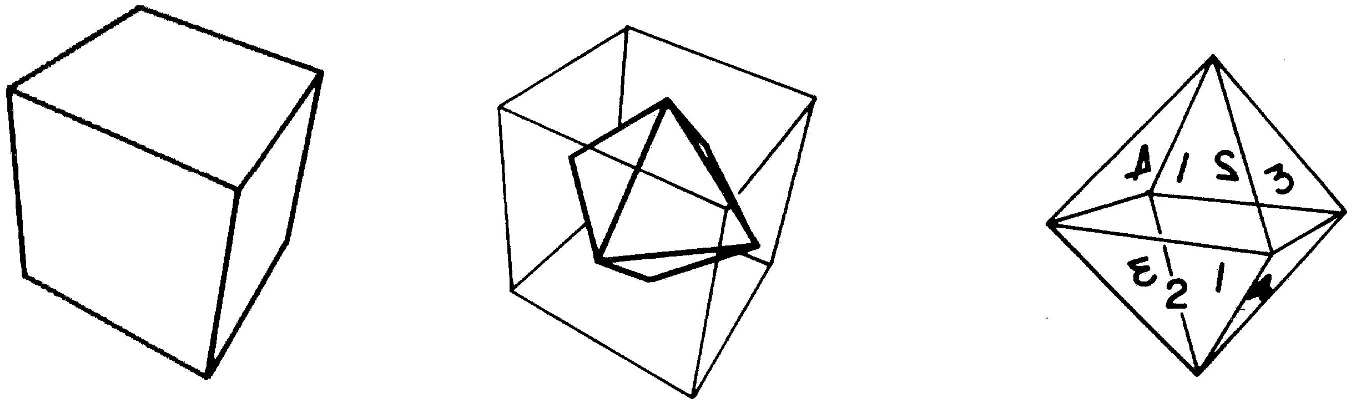


Figure 4.1.1 Objects having octahedral (O) symmetry. (a) The cube or hexahedron. (b) The octahedron. The cube is transformed into the octahedron by placing vertices of one in the center of the faces of the other. (c) (4! = 24) permutations of four integers correspond to the 24 equivalent positions in which the octahedron may be placed.

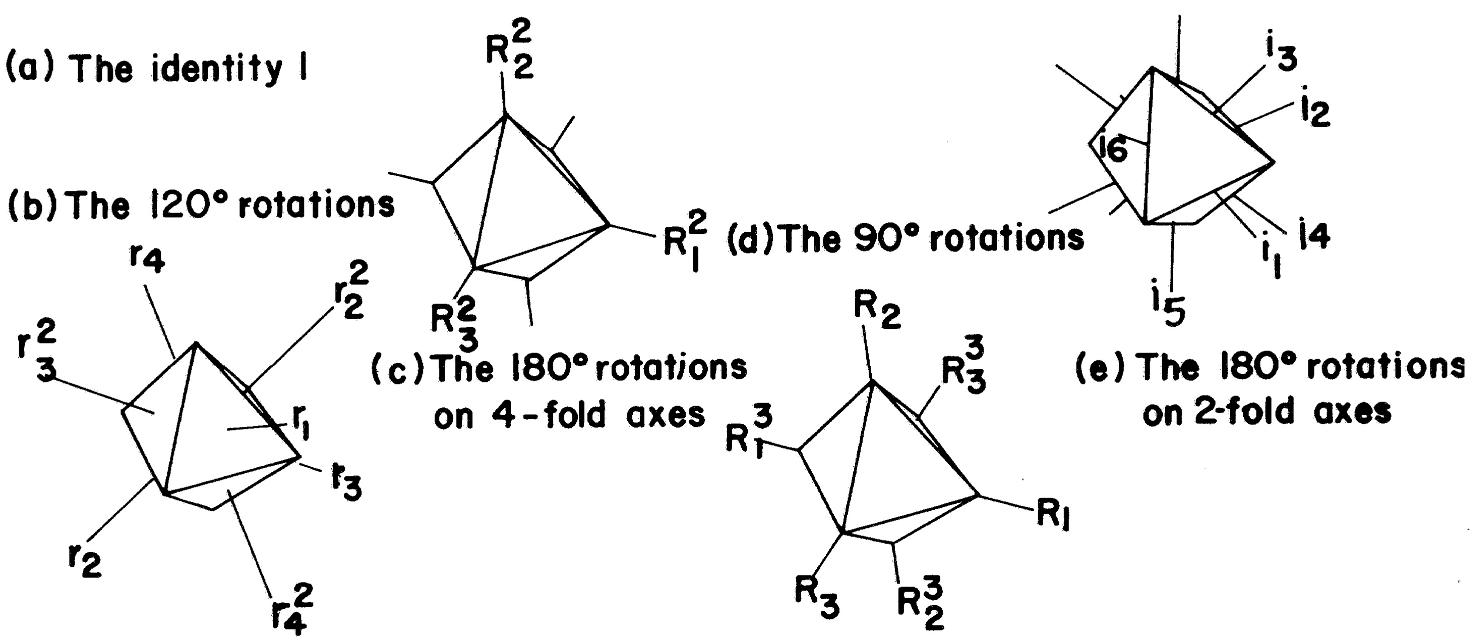


Figure 4.1.2 The five classes of octahedral operations. (a) The identity class (no rotation). (b) The threefold rotations (120°). (c) The tetragonal twofold rotations (180°). (d) The fourfold rotations (90°). (e) The diagonal twofold rotations (180°).

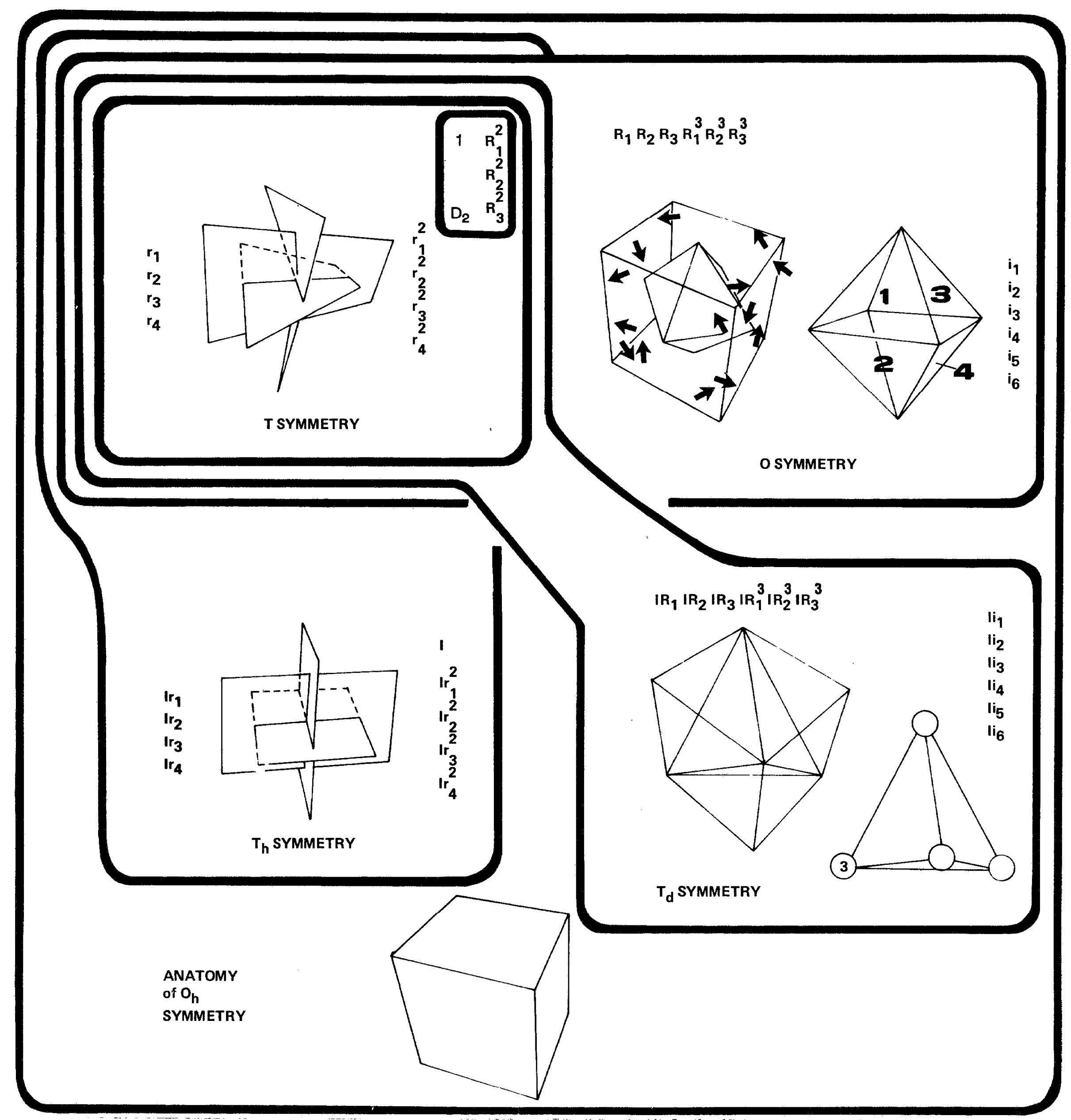


Figure 4.1.5 The full octahedral group (O_h) and four non-Abelian subgroups T, T_h, T_d, and O. The Abelian D_2 subgroup of T is indicated also.

$\ell^{A_1} = 1$

$\ell^{A_2} = 1$

$\ell^{E} = 2$

$\ell^{T_1} = 3$

$\ell^{T_2} = 3$

Example: $G = O$

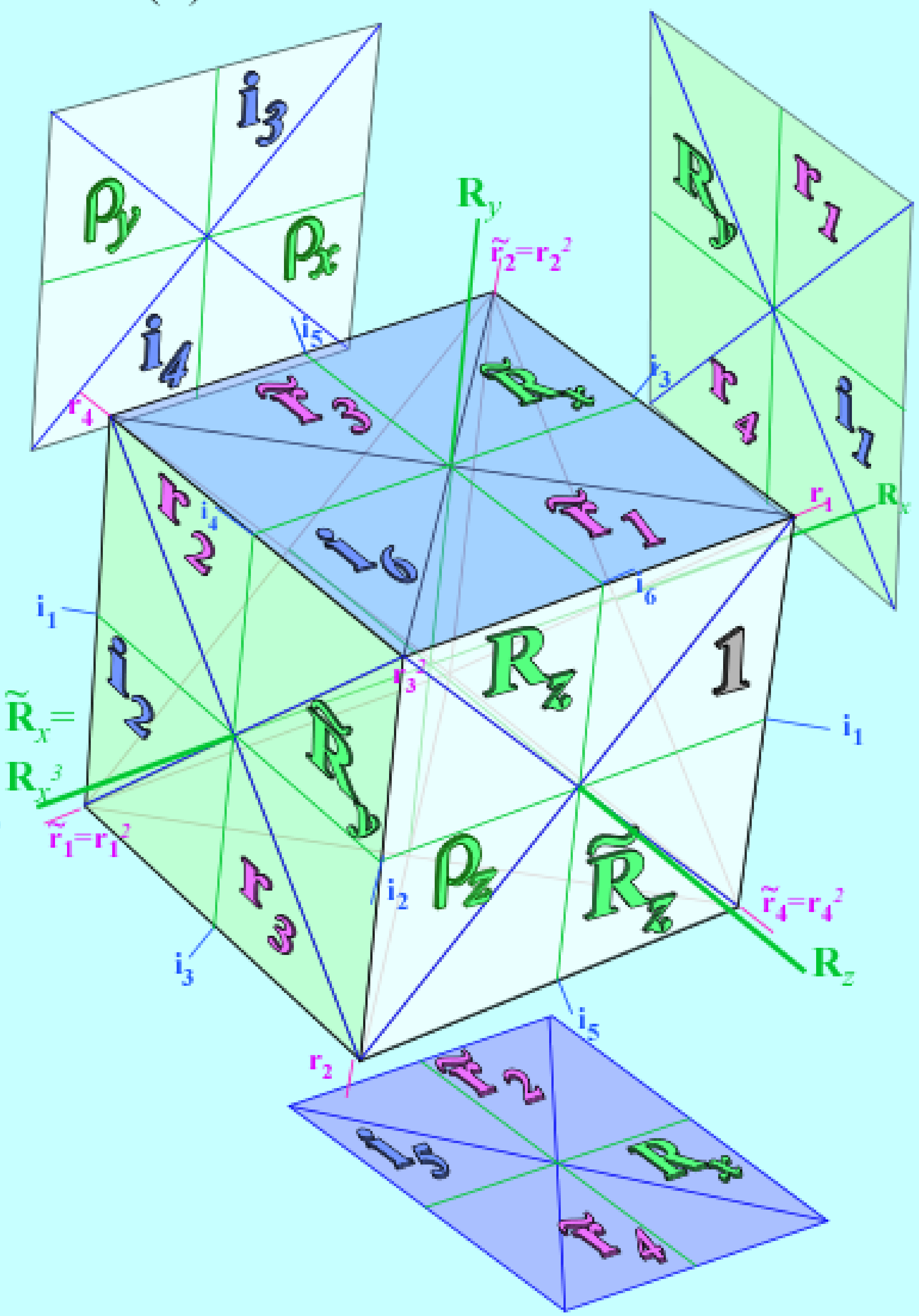
Cubic-Octahedral Group O

Centrum: $\kappa(O) = \Sigma_{(\alpha)} (\ell^{\alpha})^{0} = 1^{0} + 1^{0} + 2^{0} + 3^{0} + 3^{0} = 5$

Rank: $\rho(O) = \Sigma_{(\alpha)} (\ell^{\alpha})^{1} = 1^{1} + 1^{1} + 2^{1} + 3^{1} + 3^{1} = 10$

Order: $^{o}(O) = \Sigma_{(\alpha)} (\ell^{\alpha})^{0} = 1^{2} + 1^{2} + 2^{2} + 3^{2} + 3^{2} = 24$

	O group $\chi^{\alpha}_{\kappa_g}$	$g = 1$	r_{1-4} $\tilde{r}_{1-4}$	ρ_{xyz}	R_{xyz} $\tilde{R}_{xyz}$	i_{1-6}
s-orbital r^2	$\alpha = A_1$	1	1	1	1	1
	A_2	1	1	1	−1	−1
d-orbitals $\{x^2+y^2-2z^2, x^2-y^2\}$	E	2	−1	2	0	0
p-orbitals $\{x, y, z\}$	T_1	3	0	−1	1	−1
$\{xz, yz, xy\}$ d-orbitals	T_2	3	0	−1	−1	1



$O \supset C_4$

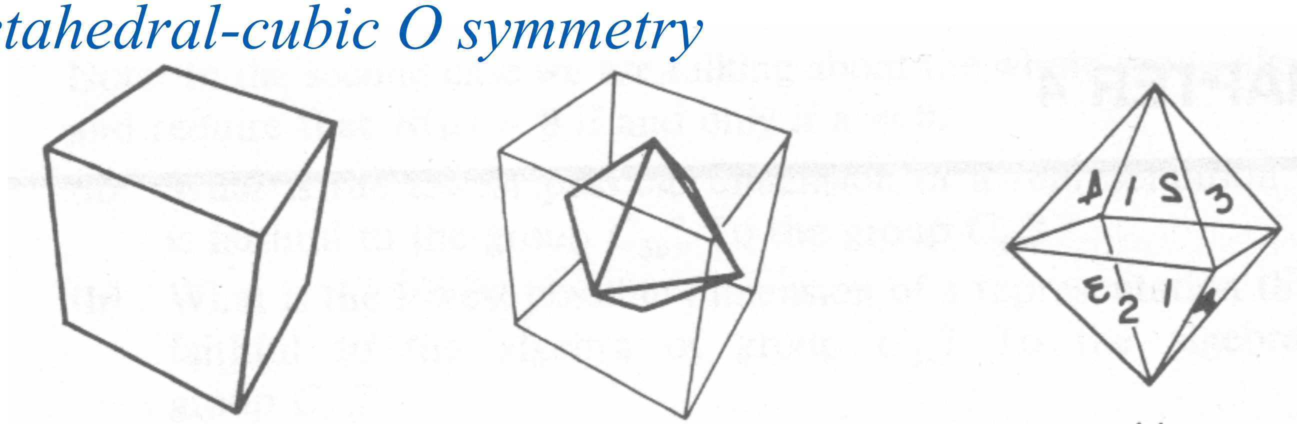
	$(0)_4$	$(1)_4$	$(2)_4$	$(3)_4=(-1)_4$
A_1	1	•	•	•
A_2	•	•	1	•
E	1	•	1	•
T_1	1	1	•	1
T_2	•	1	1	1

$O \supset C_3$

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

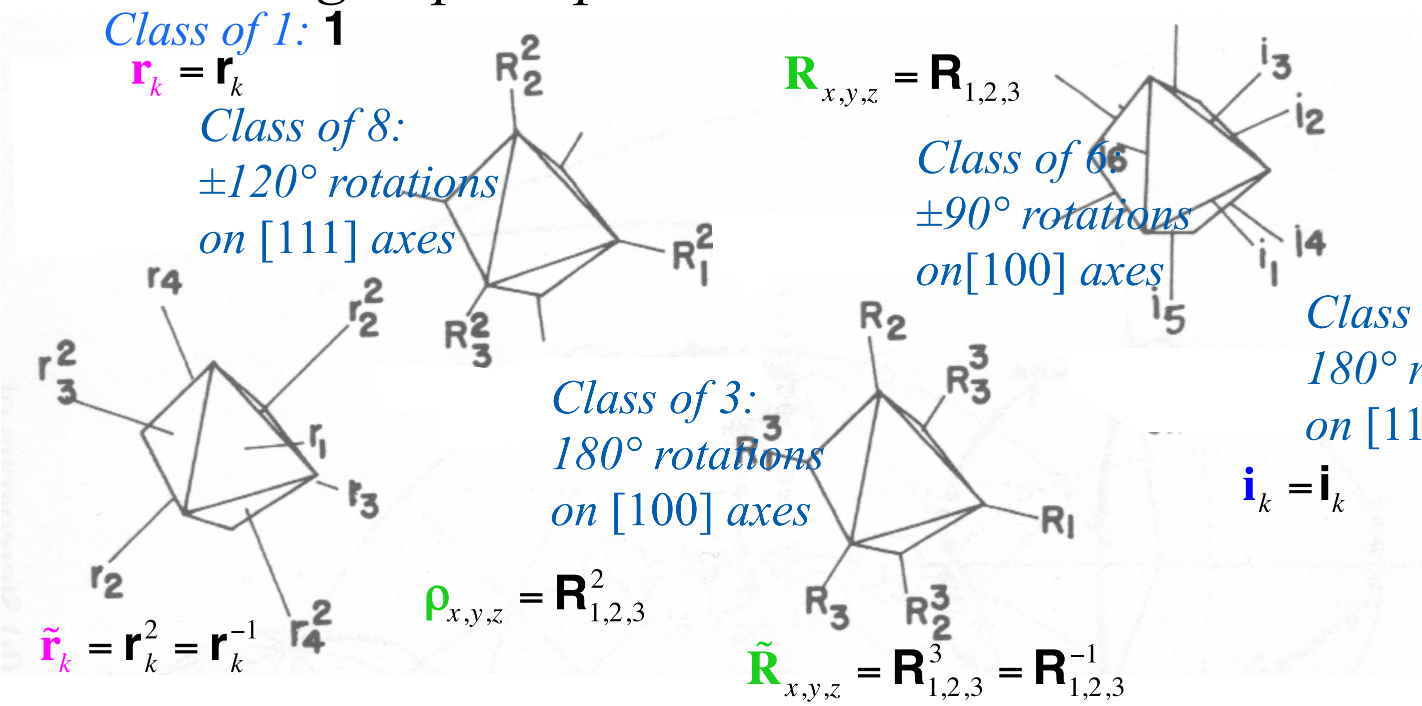
Introduction to octahedral/ tetrahedral symmetry $O_h \supset O \sim T_d \supset T$

Octahedral-cubic O symmetry



Order °O=6 hexahedron squares · 4 pts =24
=8 octahedron triangles · 3 pts =24
=12 lines · 2 pts =24 positions

Octahedral group O operations



Class of 1: **1**

$\mathbf{r}_k = \mathbf{r}_k$

Class of 8: ±120° rotations on [111] axes

$\tilde{\mathbf{r}}_k = \mathbf{r}_k^2 = \mathbf{r}_k^{-1}$

Class of 3: 180° rotations on [100] axes

$\rho_{x,y,z} = \mathbf{R}_{1,2,3}^2$

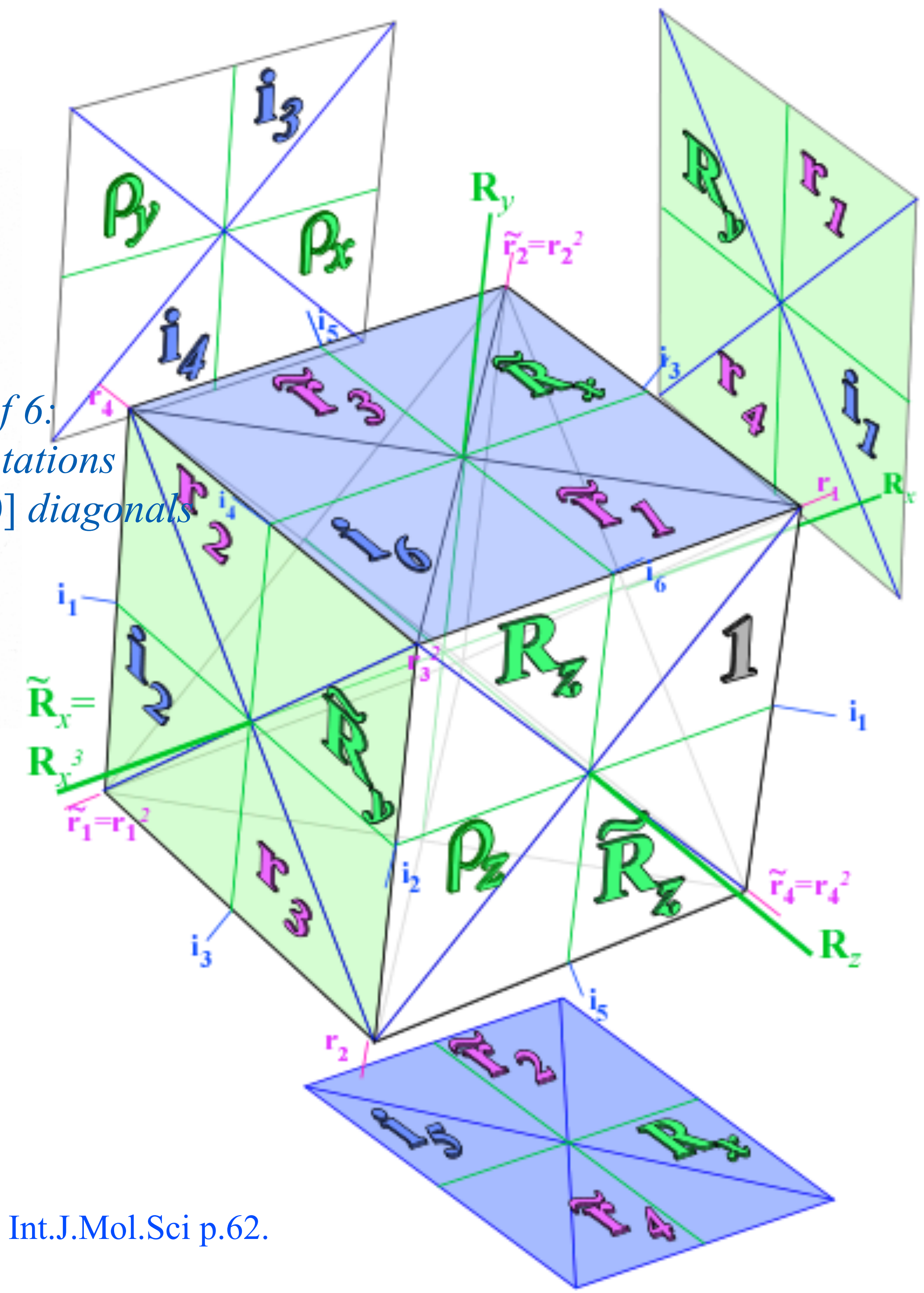
$\mathbf{R}_{x,y,z} = \mathbf{R}_{1,2,3}$

Class of 6s: ±90° rotations on[100] axes

$\tilde{\mathbf{R}}_{x,y,z} = \mathbf{R}_{1,2,3}^3 = \mathbf{R}_{1,2,3}^{-1}$

Class of 6: 180° rotations on [110] diagonals

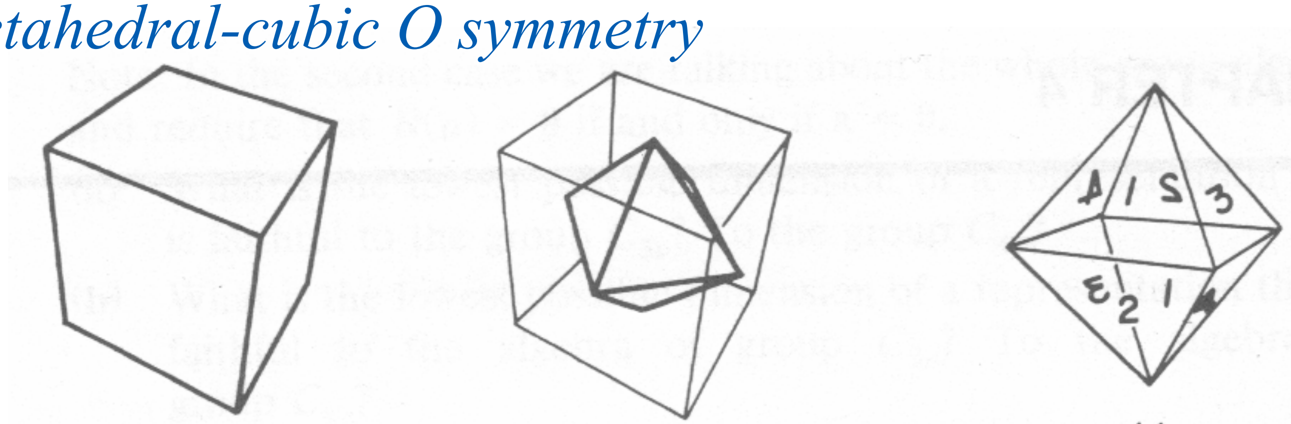
$\mathbf{i}_k = \mathbf{i}_k$



Int.J.Mol.Sci p.62.

Introduction to octahedral/ tetrahedral symmetry $O_h \supset O \sim T_d \supset T$

Octahedral-cubic O symmetry



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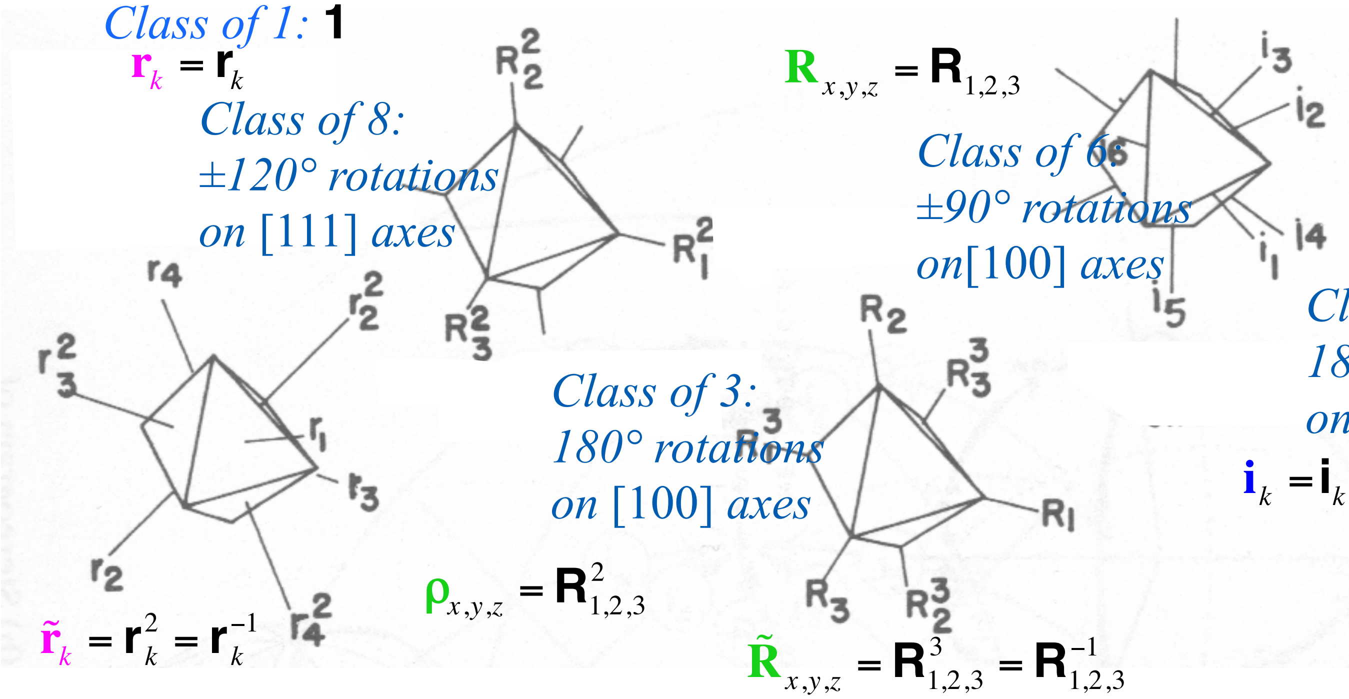
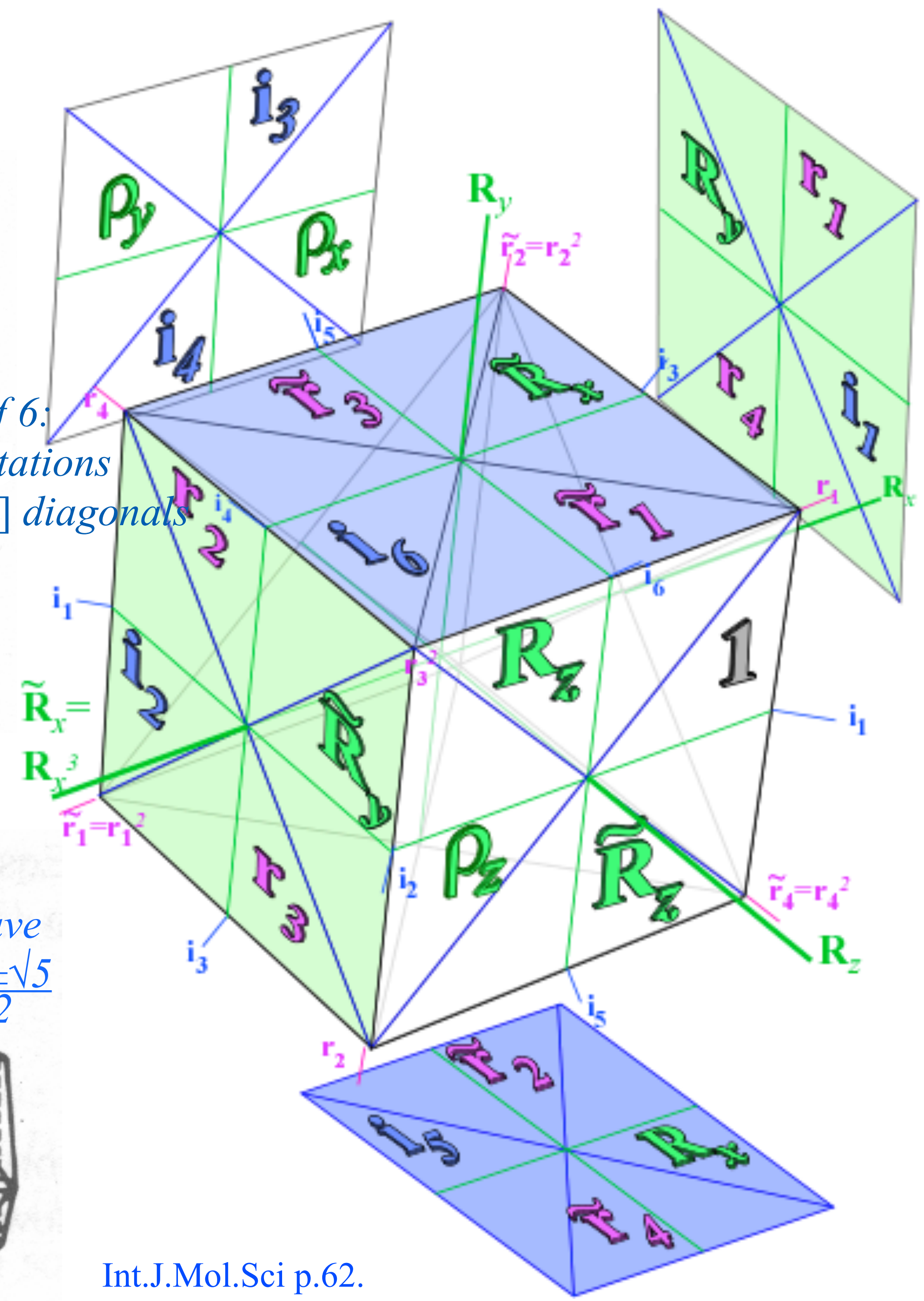
=8 octahedron triangles · 3 pts =24
=12 lines · 2 pts =24 positions

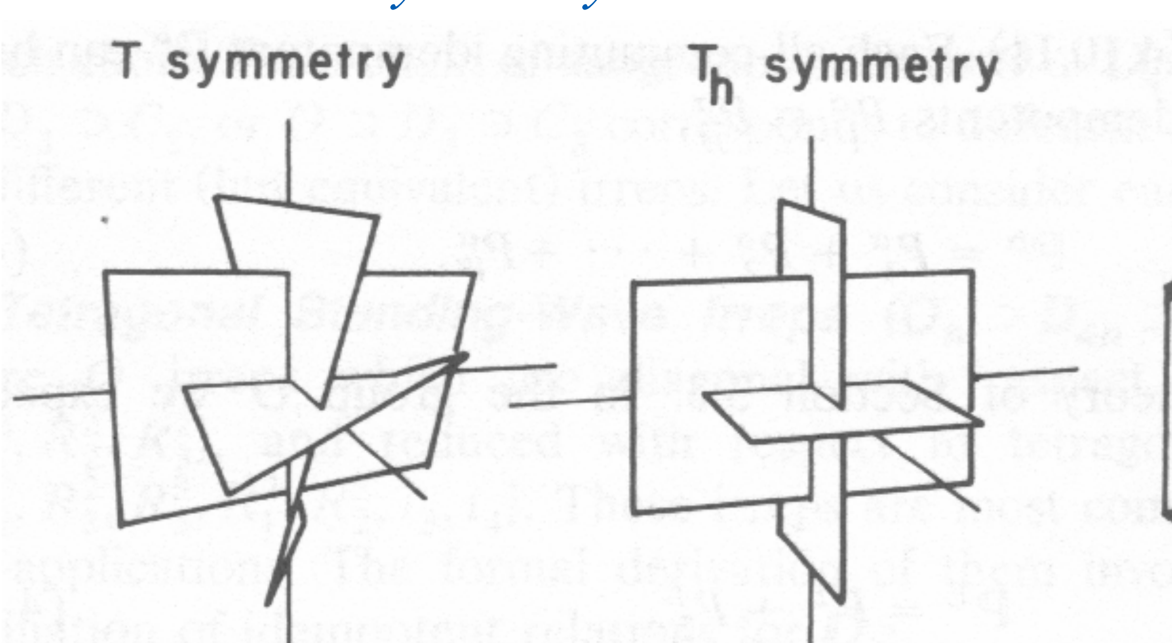
Octahedral group O operations





Int.J.Mol.Sci p.62.

Tetrahedral symmetry becomes Icosahedral



(If rectangles have Golden Ratio $\frac{1\pm\sqrt{5}}{2}$

Introduction to octahedral tetrahedral symmetry $O_h \supset O \sim T_d \supset T$

Octahedral groups $O_h \supset O \sim T_d$ and $O_h \supset T_h \supset T$

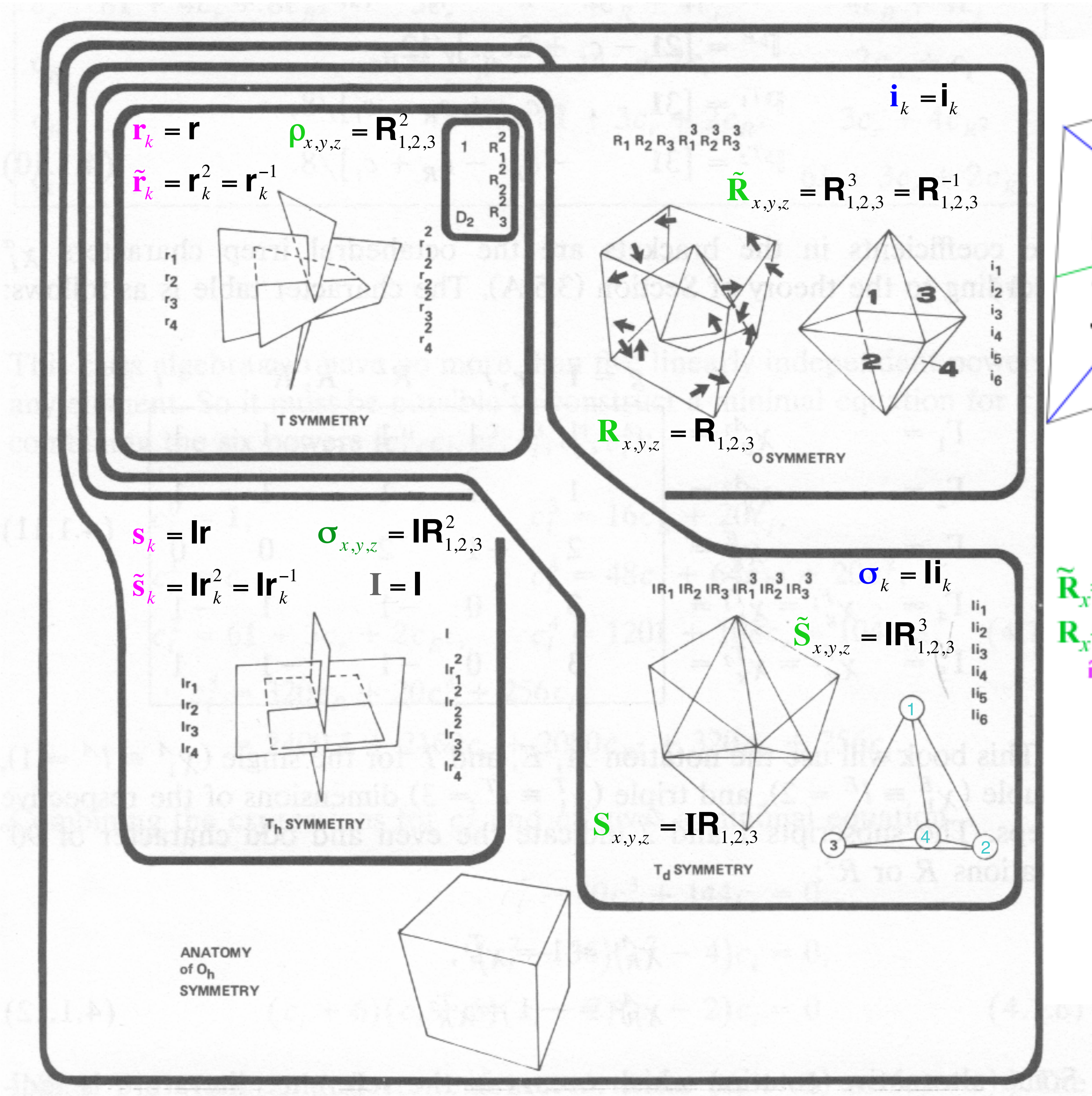
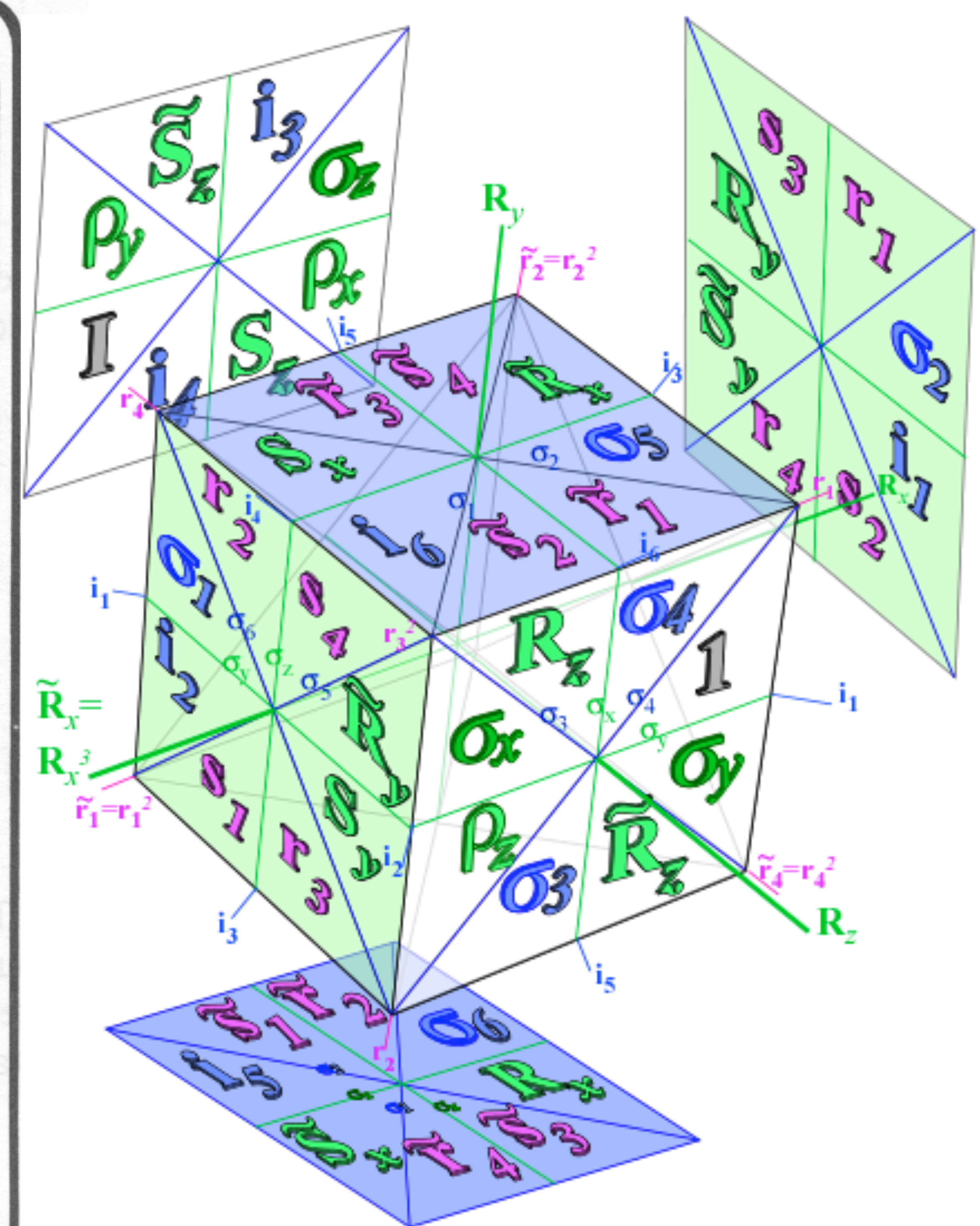


Figure 4.1.5 The full octahedral group (O_h) and four non-Abelian subgroups T, T_h, T_d, and O. The Abelian D_2 subgroup of T is indicated also.

Fig. 4.1.5 from Principles of Symmetry, Dynamics and Spectroscopy



Int.J.Mol.Sci p.63.

AMOP reference links on pages 2-4

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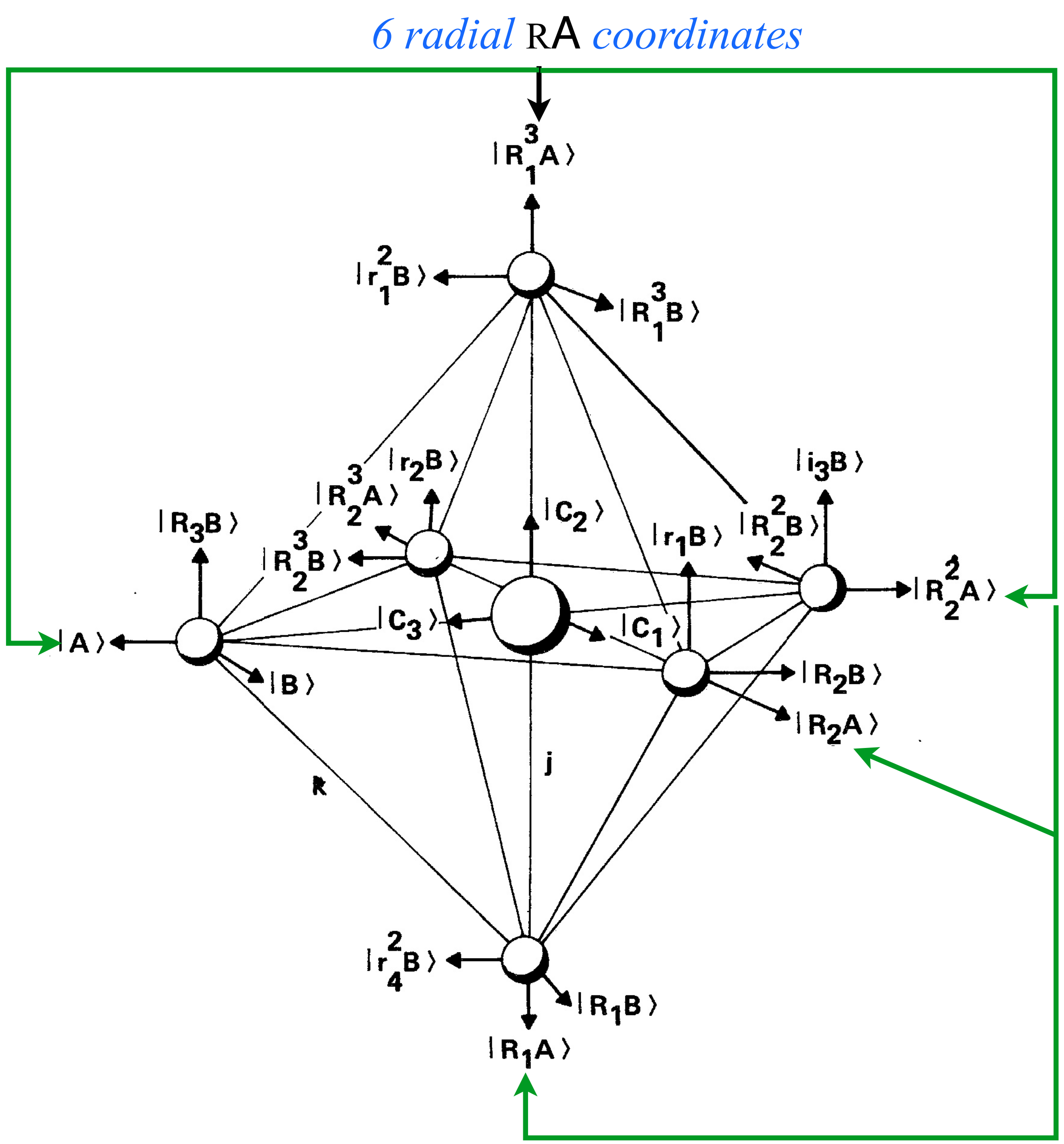
SF_6 octahedral ($O_h \supset O \supset C_{4v}$) Cartesian coordination



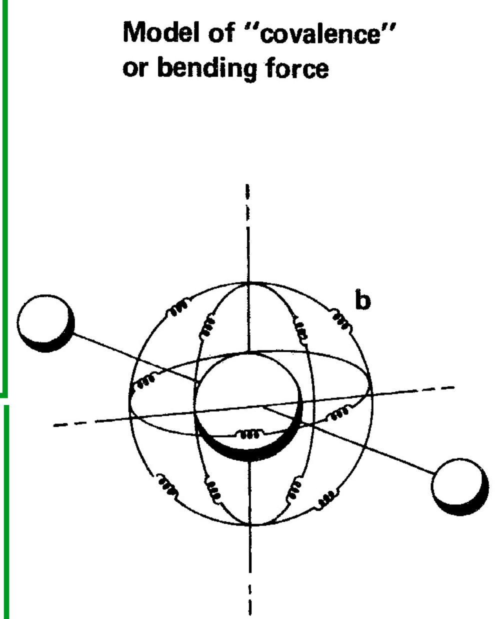
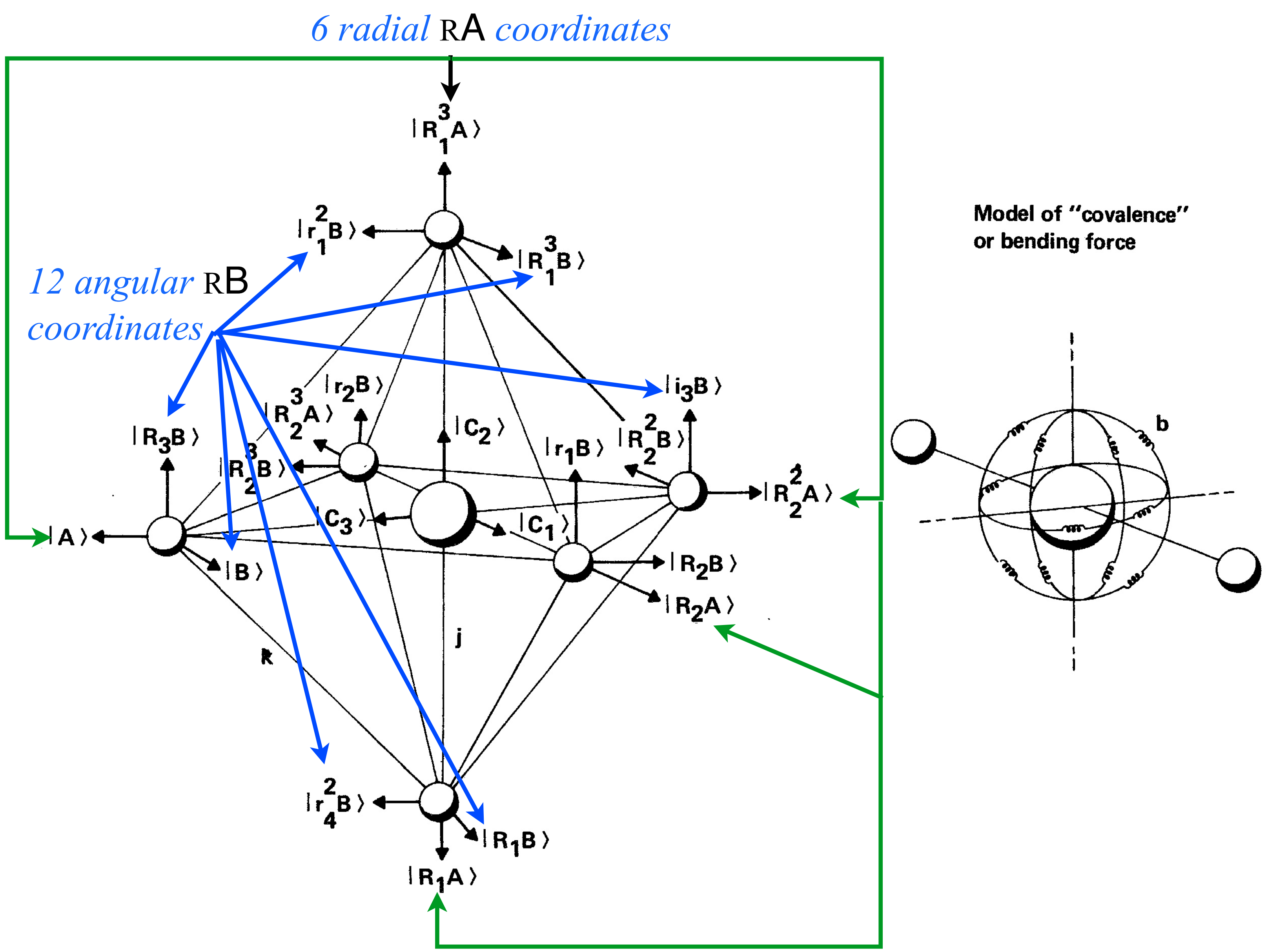


Figure 4.4.1 Octahedral hexafluoride ($UF_6, SF_6, \ldots$) molecular model Cartesian coordinates for each atom are labeled by orbit (A, B, or C) and coset leaders. ($\mathbf{1} = R_3, r_1, R_2, \ldots$ etc.) Spring constants are equal to (k) for (F—F) bonds and j for radial (F-central) bonds. Bending spring constant is b.

SF_6 octahedral ($O_h \supset O \supset C_{4v}$) Cartesian coordination



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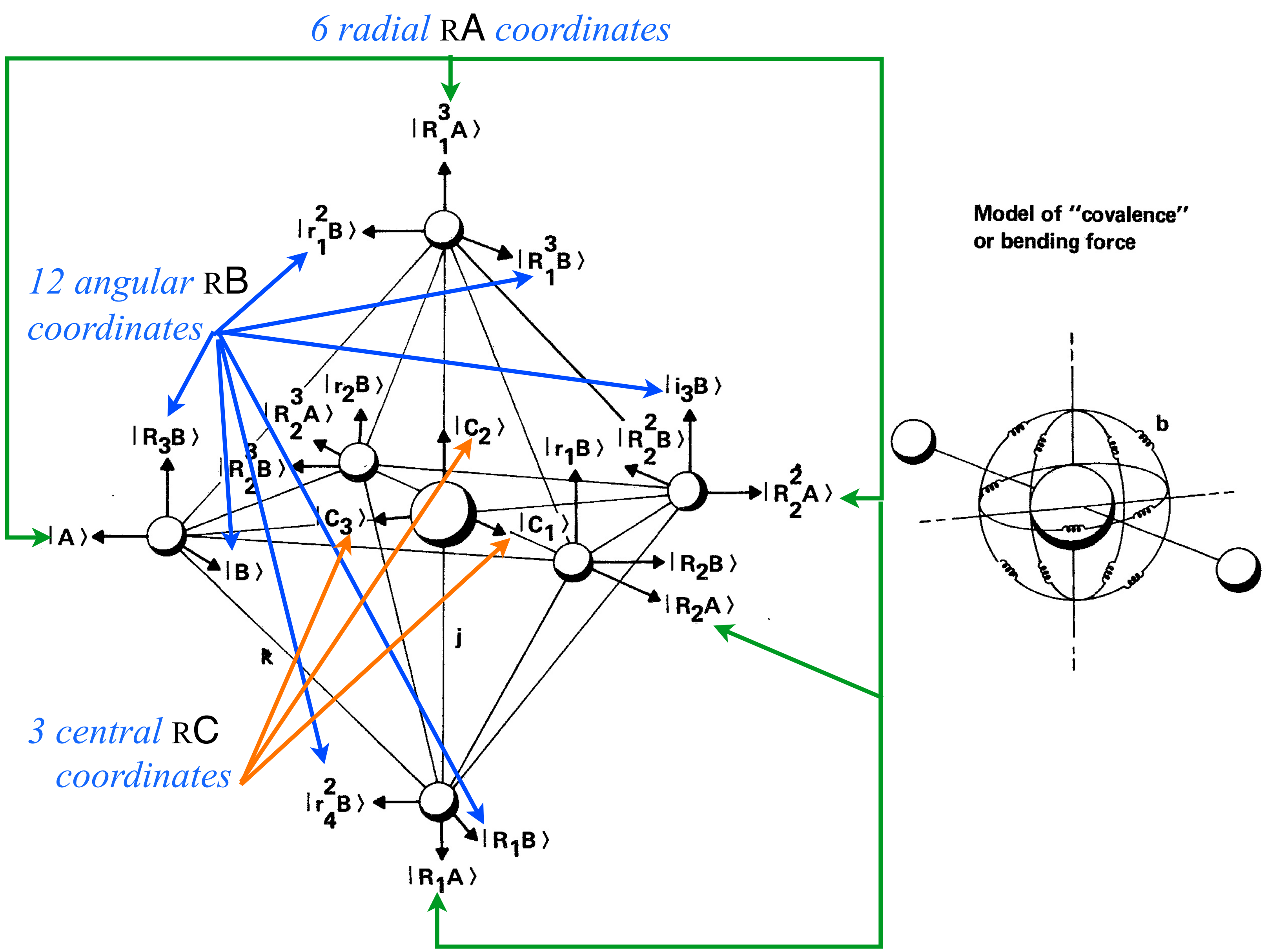

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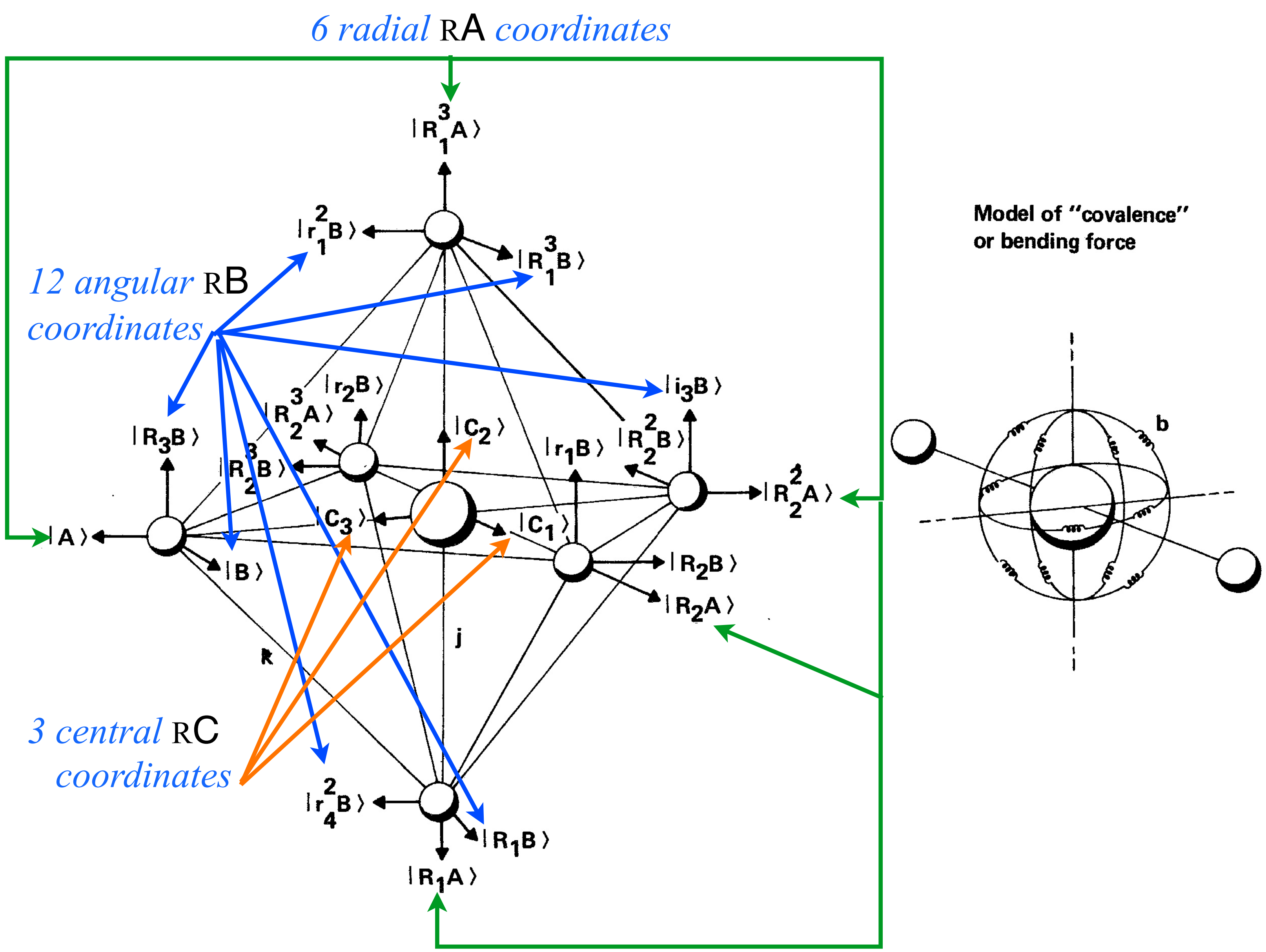

6 radial RA
12 angular RB
+3 central RC
= 21 total dimension

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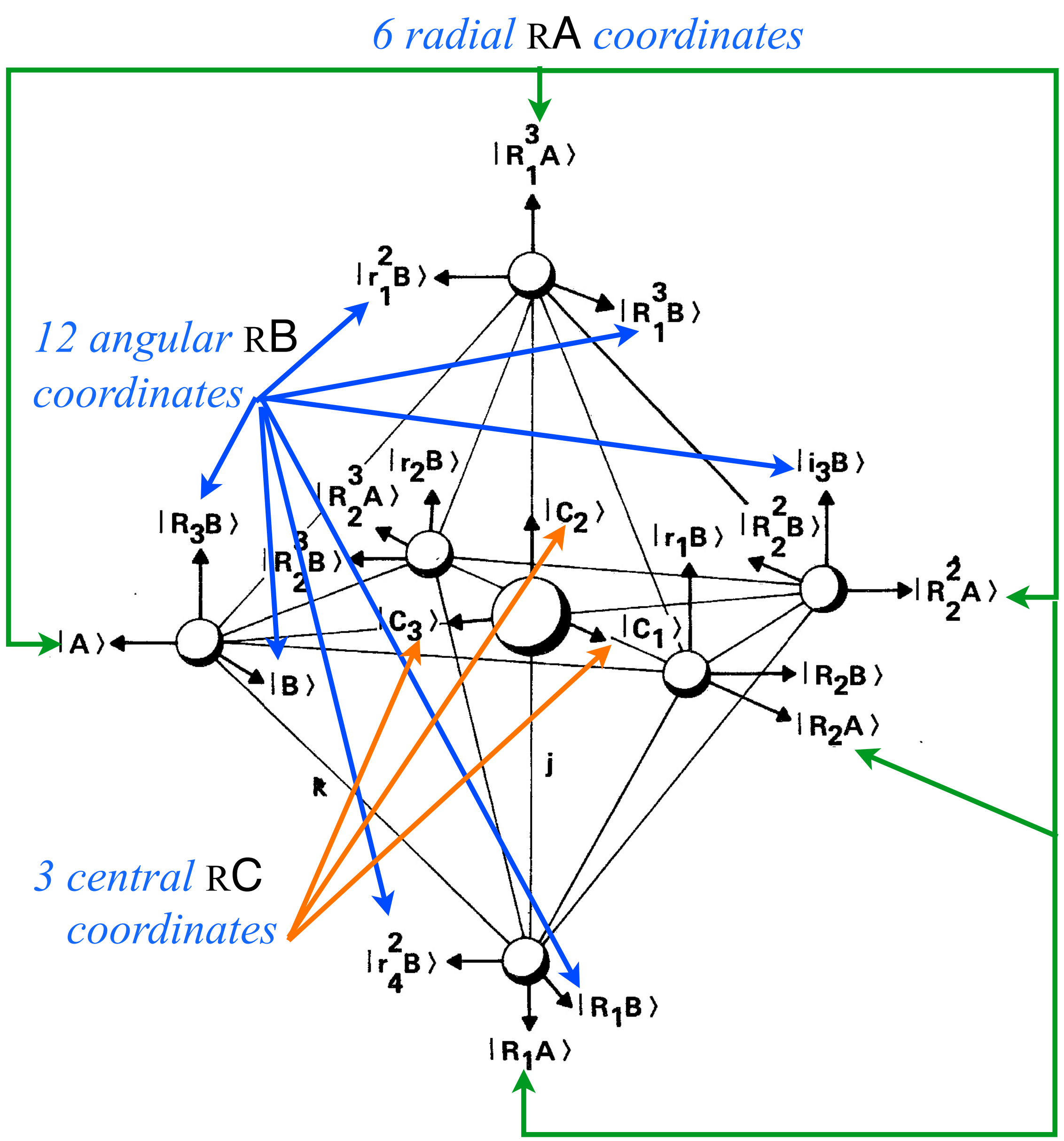

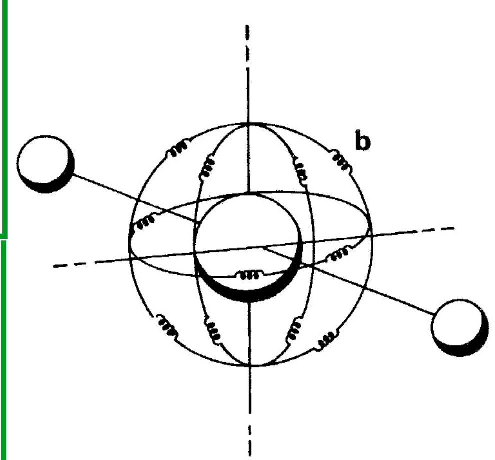

6 radial RA
12 angular RB
+*3 central* RC
= 21 total dimension
- 3 T_{1u} translations (polar-vector)
- 3 T_{1g} rotations (axial-vector)
= 15 *genuine* modes

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O-C4v correlation *Lect.16 p.14.*

O_h radial vibrational modes based on induced representation (A_1 of C_{4v})$\uparrow O_h = A_{1g} \oplus T_{1u} \oplus E_g$

Classical vibrator model and analogous Quantum tunneling model

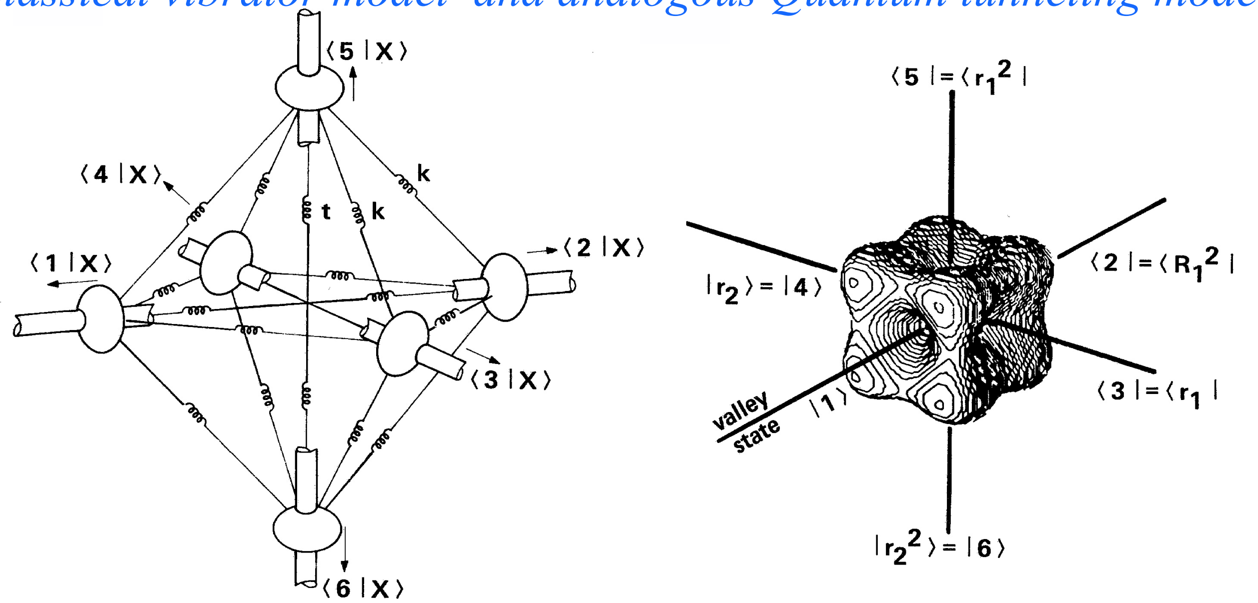

Figure 4.3.1 Examples of physical systems with octahedral symmetry. (a) Coupled oscillating beads sliding on octahedral axes are described by six classical coordinates $x_j = \langle j|x\rangle$. (b) A six-state quantum system could describe a particle capable of tunneling between six equivalent potential valleys.

O-C4v levels *Lect.16 p.79.*

subgroup correlation

$O_h \supset C_{4v}$

$O_h \supset C_{4v}$	A'	B'	A''	B''	E
$A_{1g}\downarrow C_{4v}$	1	·	·	·	·
$A_{2g}\downarrow C_{4v}$	·	1	·	·	·
$E_g\downarrow C_{4v}$	1	1	·	·	·
$T_{1g}\downarrow C_{4v}$	·	·	1	·	1
$T_{2g}\downarrow C_{4v}$	·	·	·	1	1
$A_{1g}\downarrow C_{4v}$	·	·	1	·	·
$A_{2u}\downarrow C_{4v}$	·	·	·	1	·
$E_u\downarrow C_{4v}$	·	·	1	1	·
$T_{1u}\downarrow C_{4v}$	1	·	·	·	1
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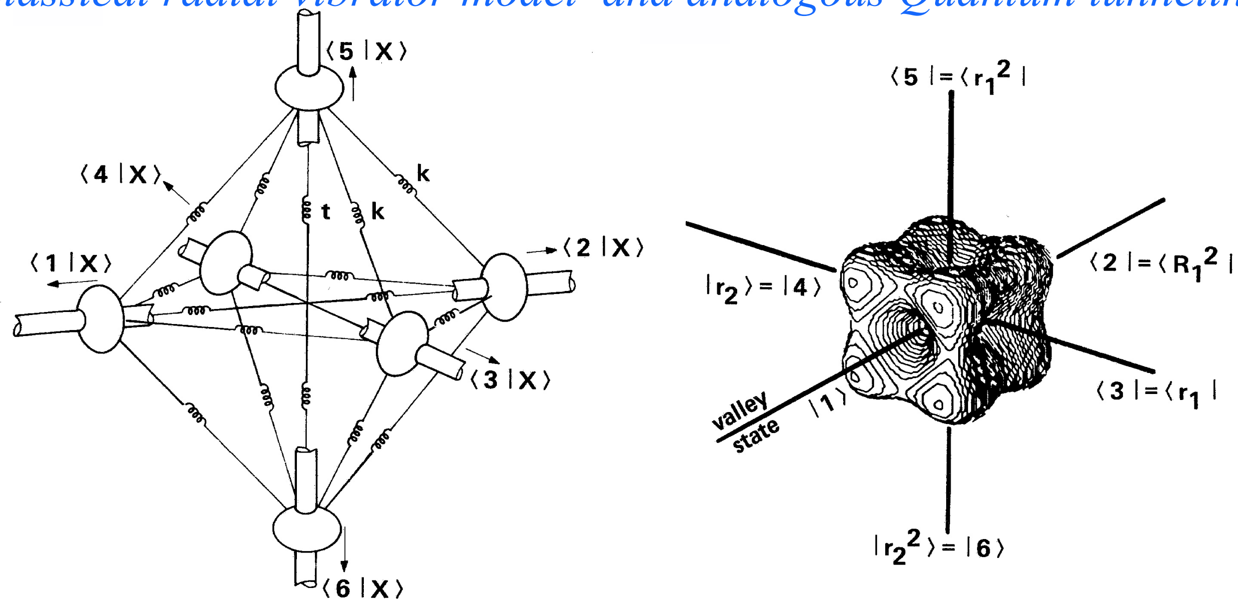

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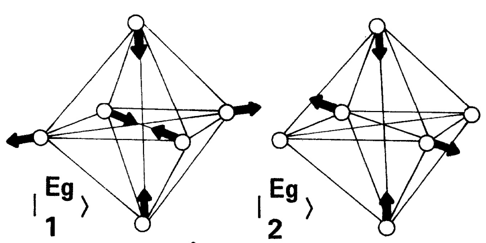
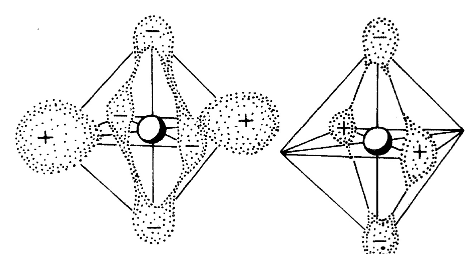
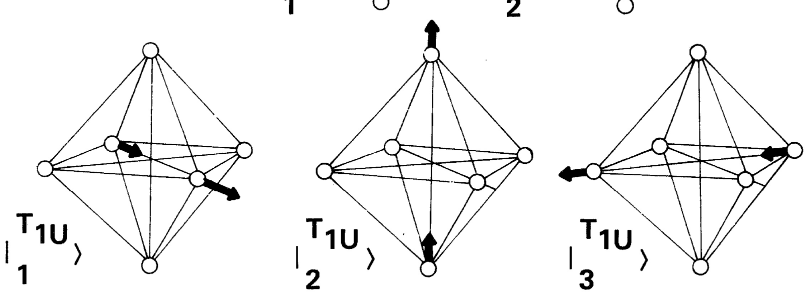
$T_{2u} \downarrow C_{4v}$	·	1	·	·	1



$2E_g$ modes

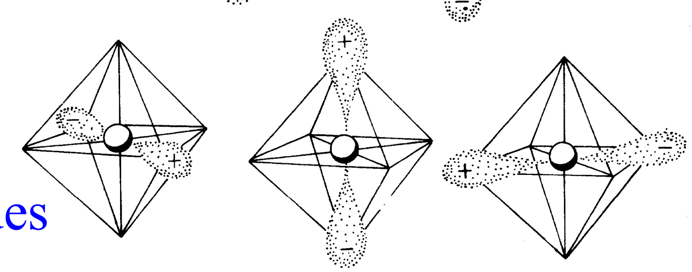
E
H − 2S

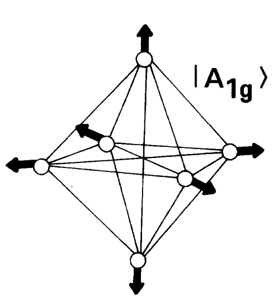




T1
H

$3T_{1u}$ modes

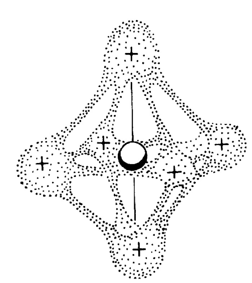




$1A_{1g}$ mode

A1
H + 4S

FREQUENCY OR ENERGY SPECTRUM



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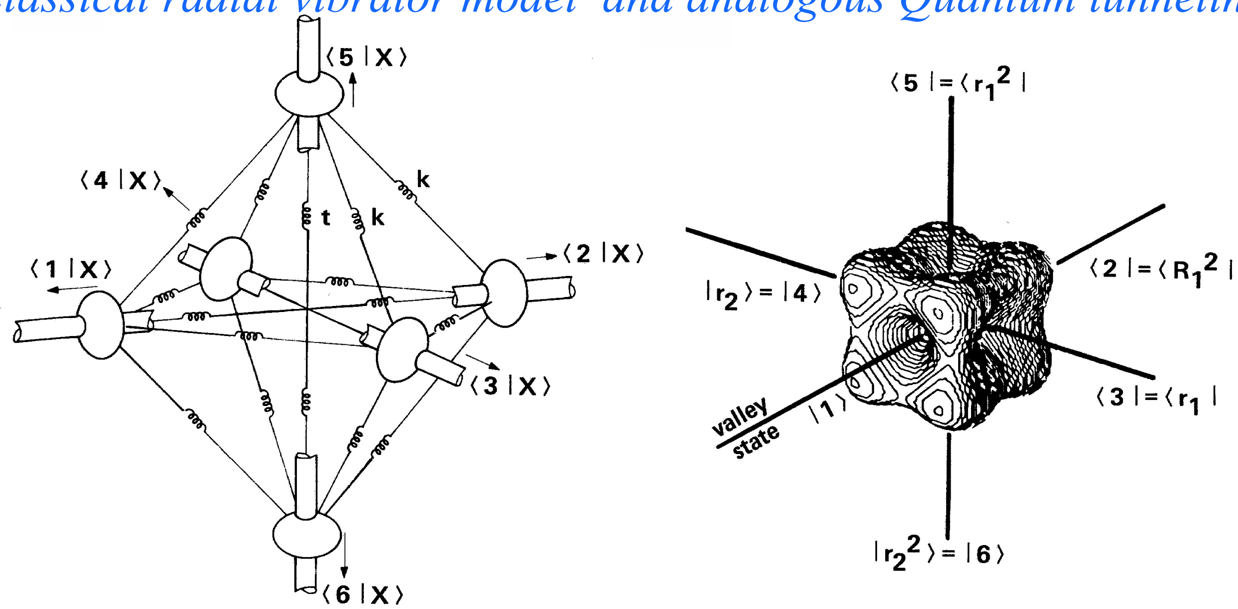

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$T_{2g} \downarrow C_{4v}$	·	·	·	1	1
$A_{1g} \downarrow C_{4v}$	·	·	1	·	·
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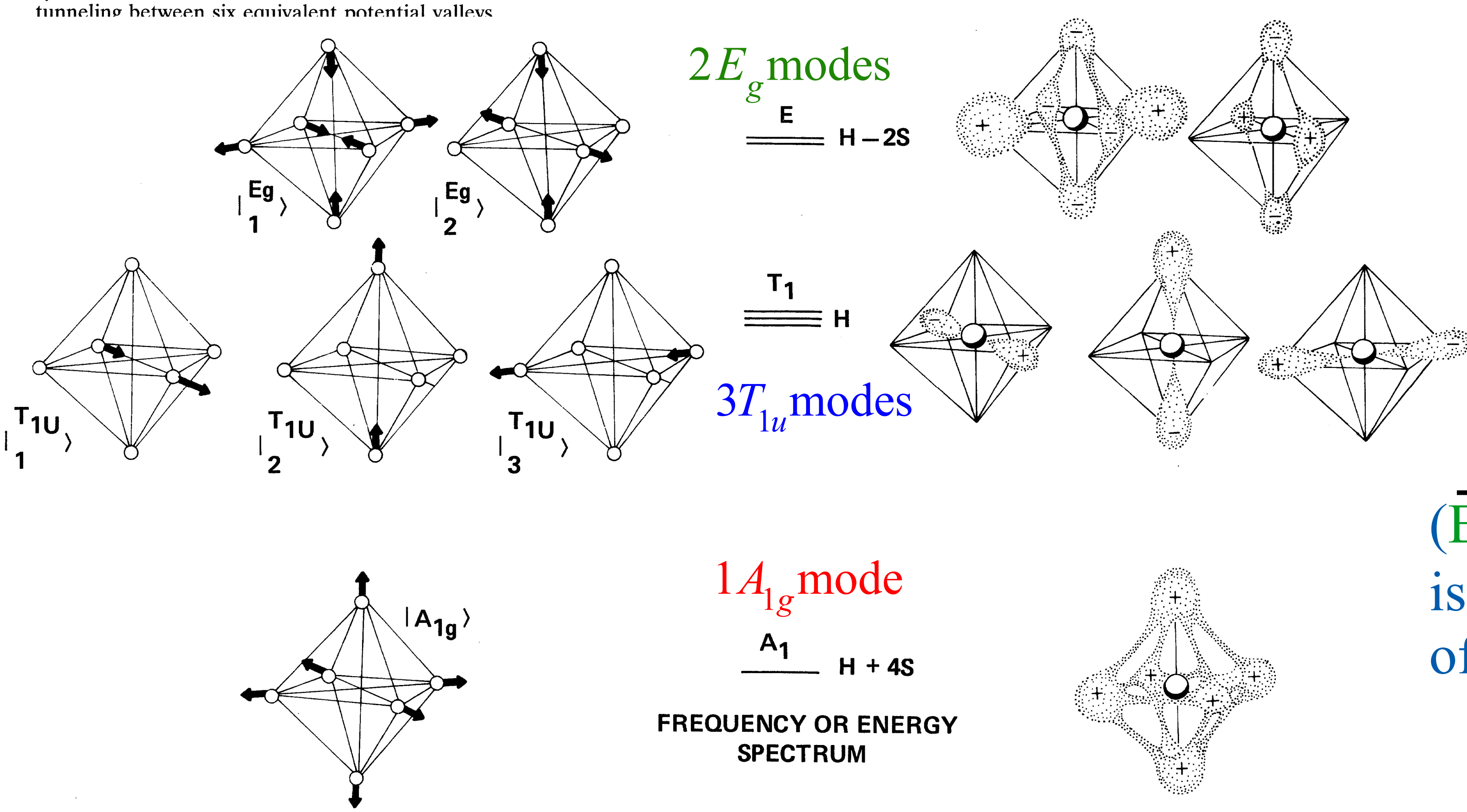

$(E$ of $C_{4v})\uparrow O_h = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$ is induced representation basis of O_h angular B vibrational modes

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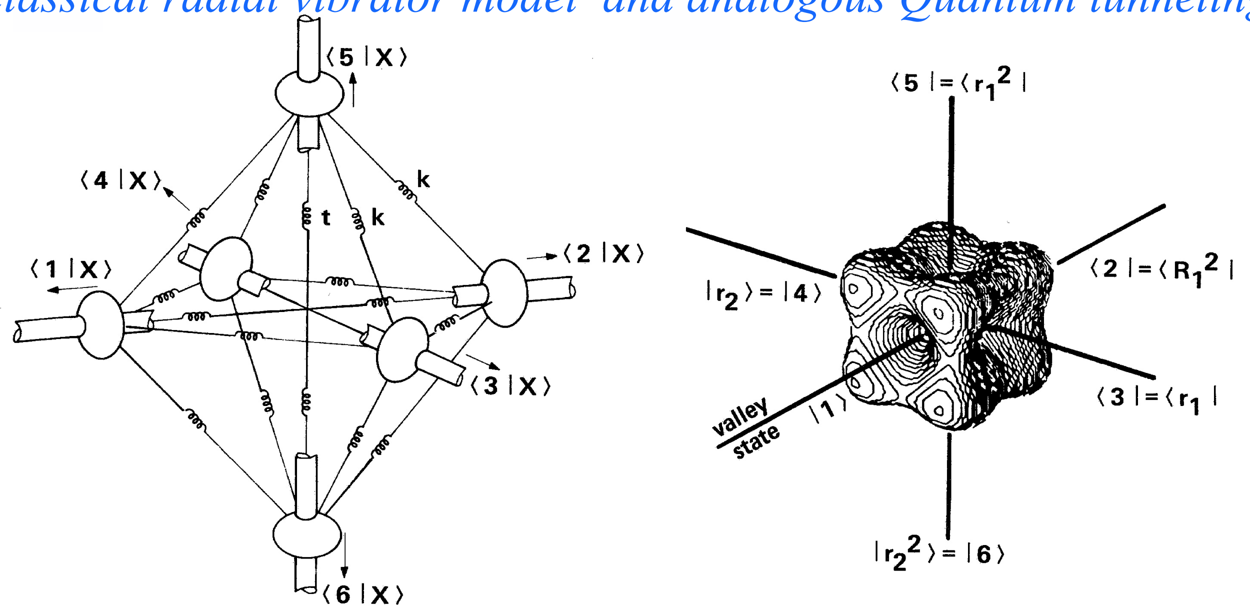

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$T_{1g} \downarrow C_{4v}$	·	·	1	·	1
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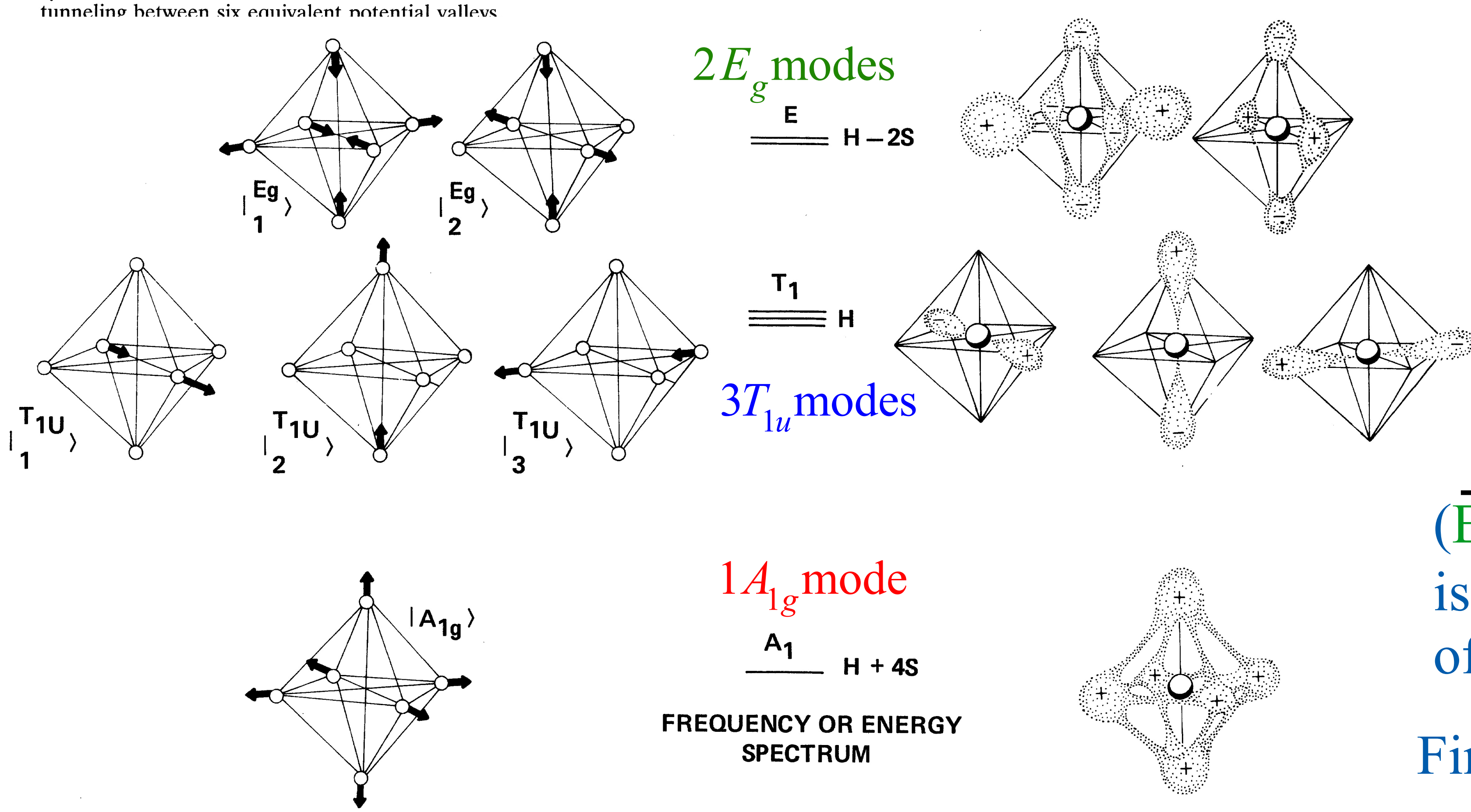

(E of C_{4v})$\uparrow O_h = T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u}$
is induced representation basis
of O_h angular B vibrational modes

Finally, O_h central C vector triplet T_{1u}

AMOP reference links on pages 2-4

4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

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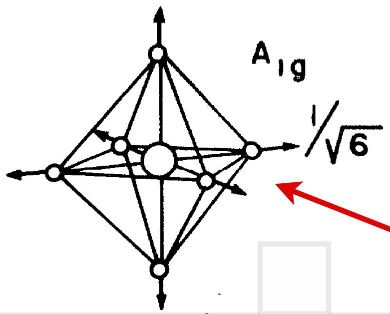

15 genuine modes need to be projected from 21 candidates in (A⊕B⊕C) collection

3 radial modes *12 angular modes* *3 central atom modes*

$$(A \oplus B \oplus C) = (A_{1g} \oplus T_{1u} \oplus E_g)_A \oplus (T_{1g} \oplus T_{2g} \oplus T_{1u} \oplus T_{2u})_B \oplus (T_{1u})_C$$

1 A_{1g} *ready to go*

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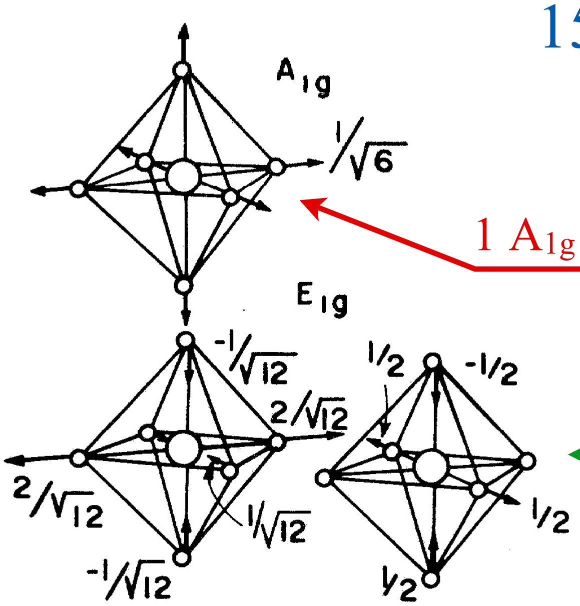

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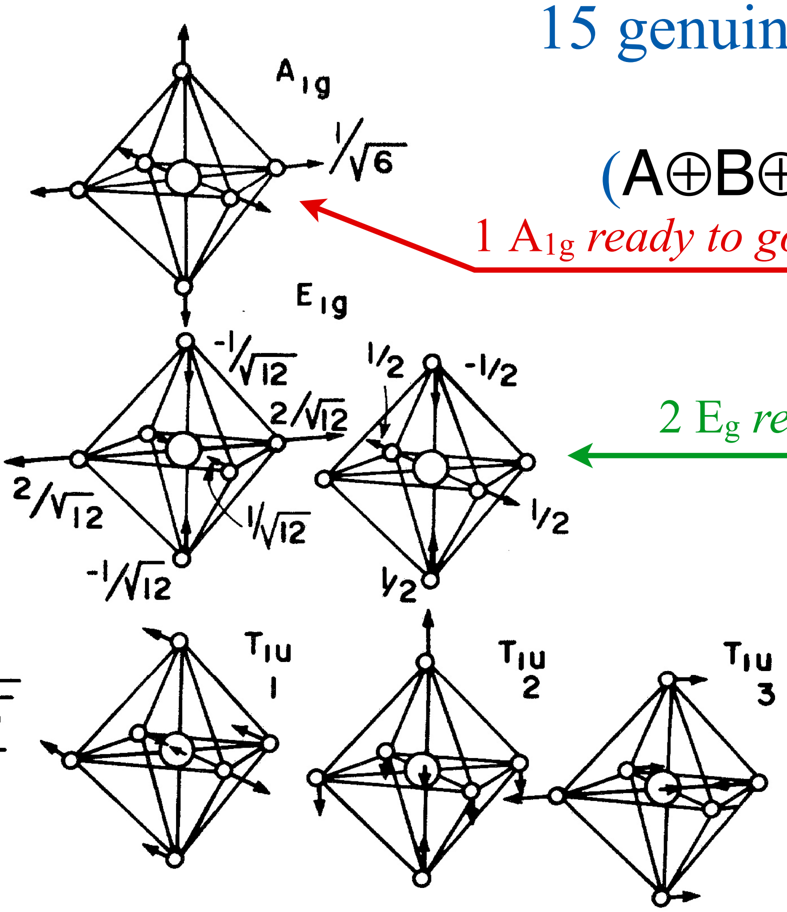

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Needs mixing with 2 other T_{1u}

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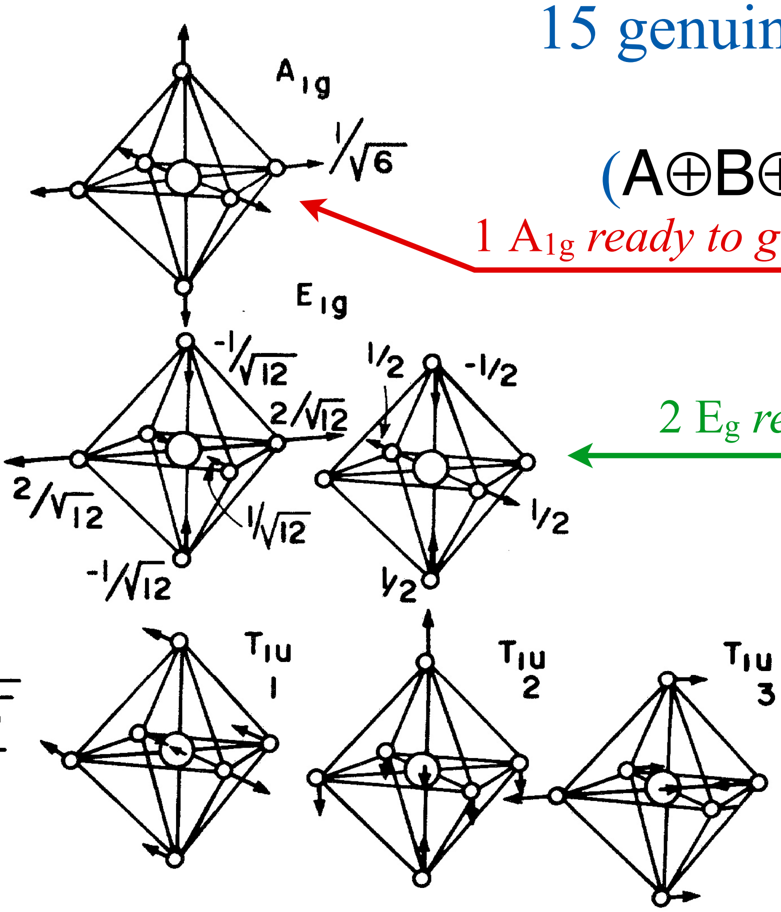

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...and translation must be discarded.

T_{1u} *translation (discarded)*

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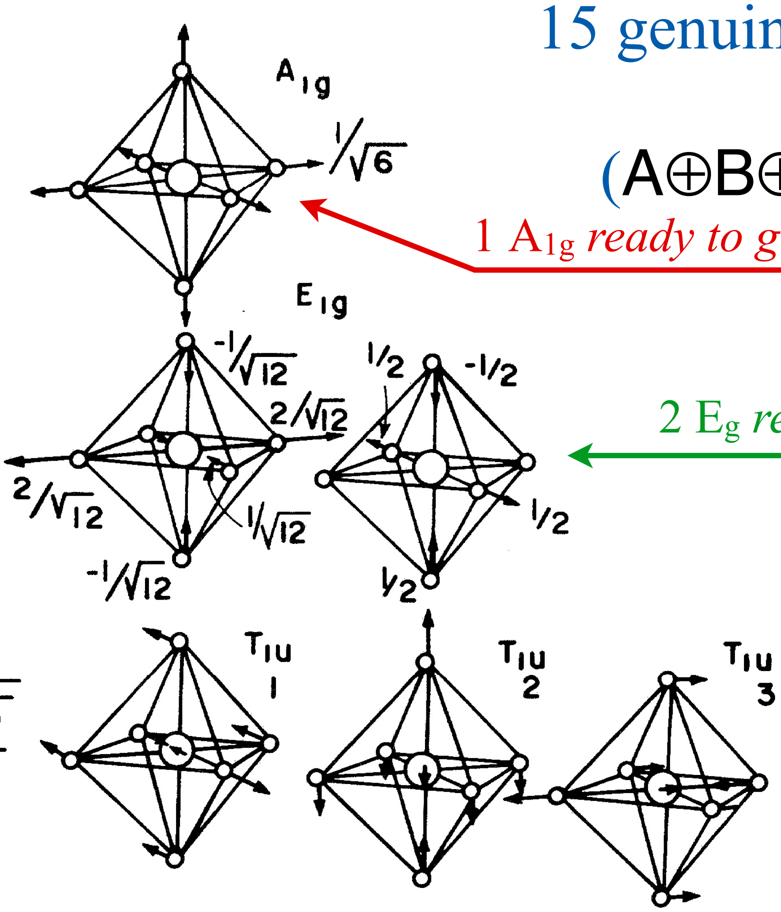

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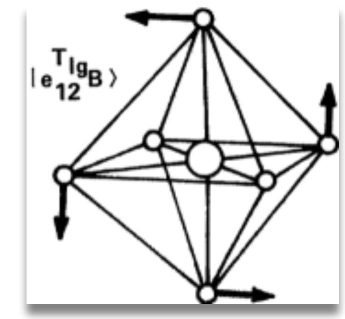

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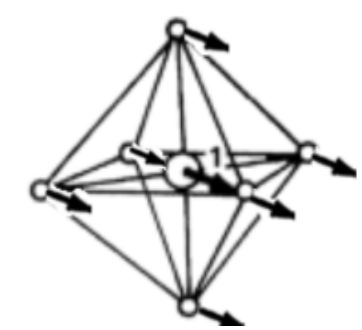

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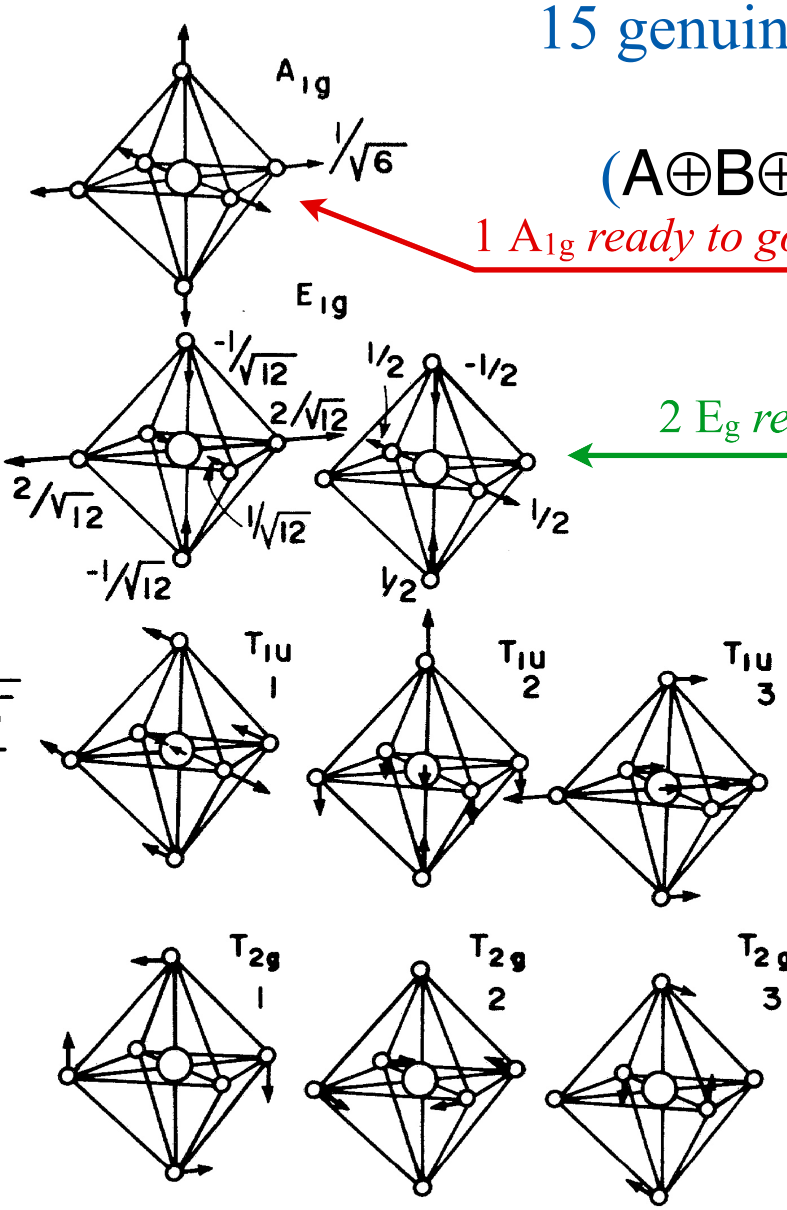

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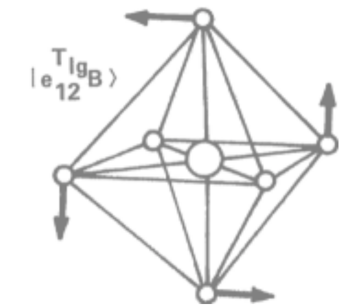

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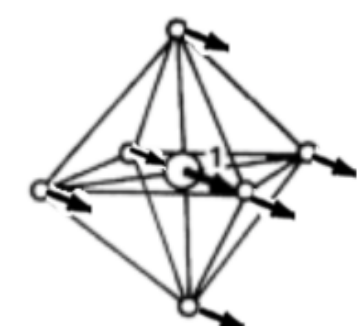

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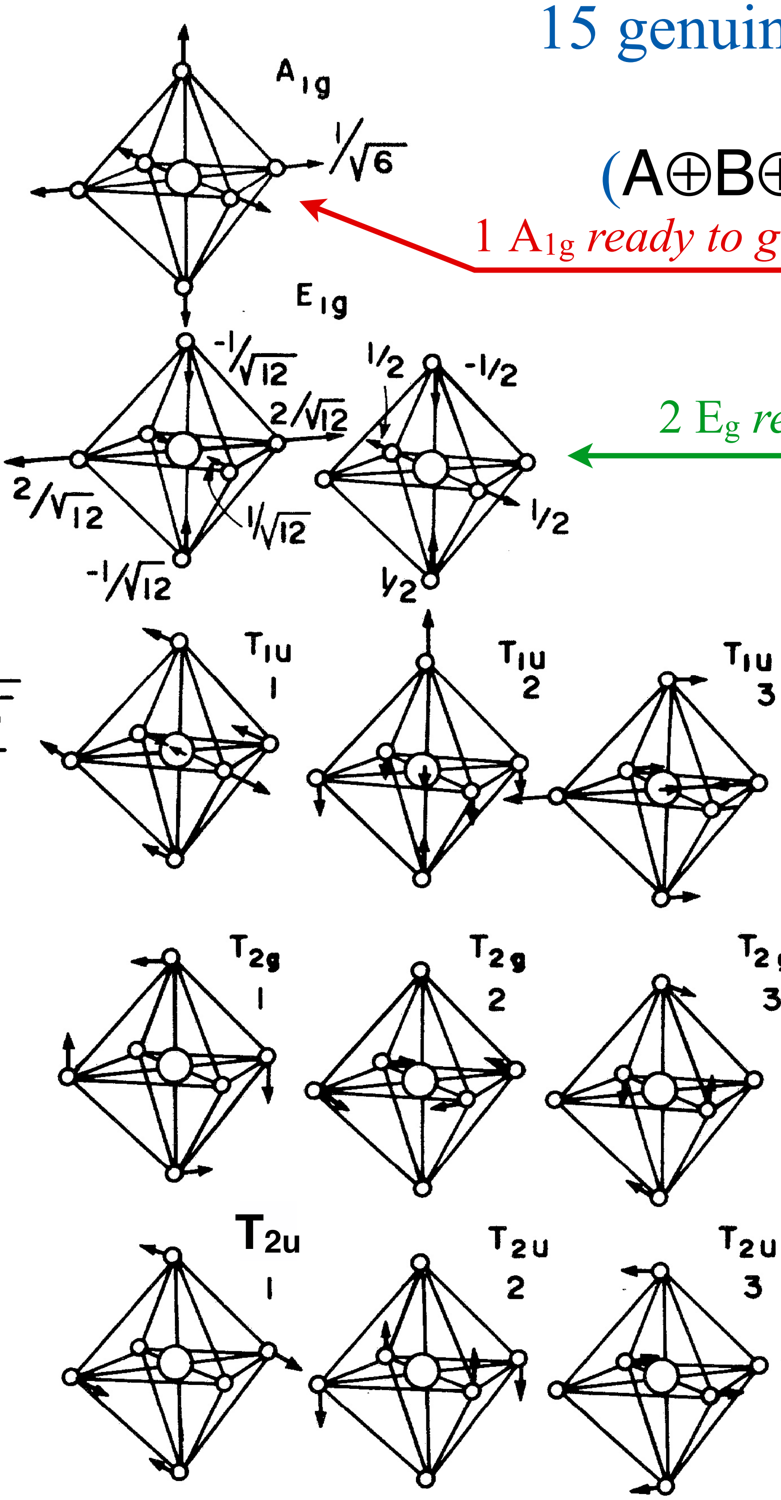

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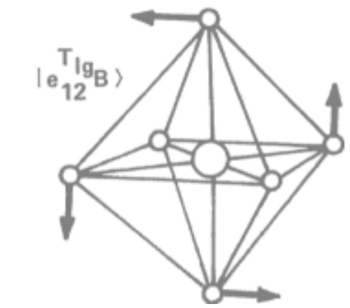

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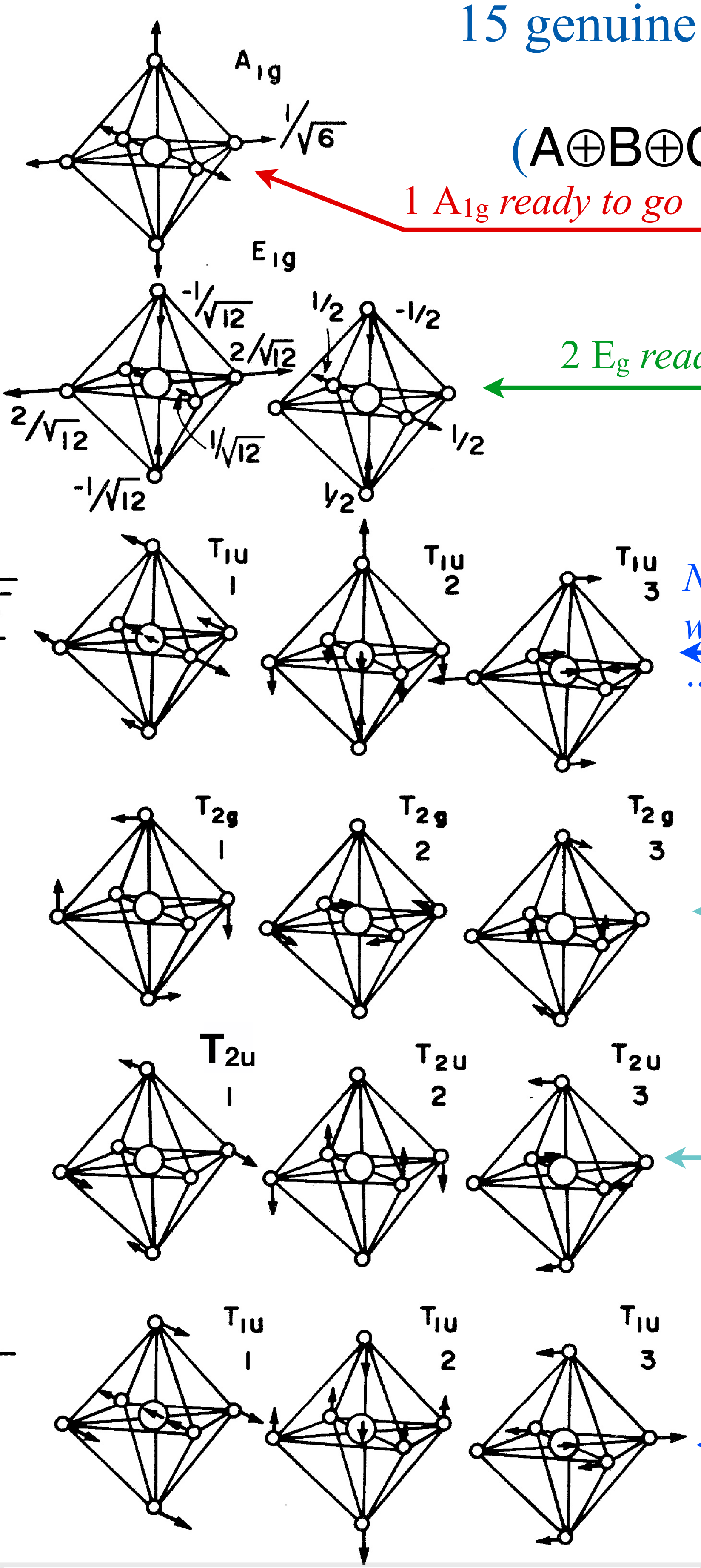

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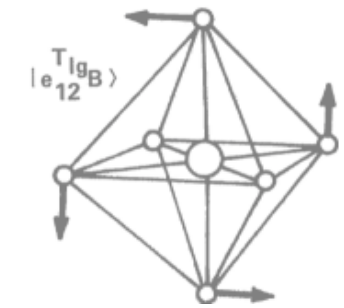

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Ireps for O⊃D_4⊃D_2 subgroup chain and coset factored projectors

T_1 *Vector* x,y,z

D_2:

$$\mathscr{D}^{T_1}(1)=\begin{vmatrix}1&\cdot&\cdot\\\cdot&1&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad R_1^2=\begin{vmatrix}1&\cdot&\cdot\\\cdot&-1&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad r_1=\begin{vmatrix}\cdot&\cdot&1\\1&\cdot&\cdot\\\cdot&1&\cdot\end{vmatrix}\quad r_2=\begin{vmatrix}\cdot&\cdot&-1\\1&\cdot&\cdot\\\cdot&-1&\cdot\end{vmatrix}\quad r_1^2=\begin{vmatrix}\cdot&1&\cdot\\\cdot&\cdot&1\\1&\cdot&\cdot\end{vmatrix}\quad r_2^2=\begin{vmatrix}\cdot&1&\cdot\\\cdot&\cdot&-1\\-1&\cdot&\cdot\end{vmatrix}$$

$$\mathscr{D}^{T_1}(R_3^2)=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&-1&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad R_2^2=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&1&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad r_4=\begin{vmatrix}\cdot&\cdot&1\\-1&\cdot&\cdot\\\cdot&-1&\cdot\end{vmatrix}\quad r_3=\begin{vmatrix}\cdot&\cdot&-1\\-1&\cdot&\cdot\\\cdot&1&\cdot\end{vmatrix}\quad r_3^2=\begin{vmatrix}\cdot&-1&\cdot\\\cdot&\cdot&1\\-1&\cdot&\cdot\end{vmatrix}\quad r_4^2=\begin{vmatrix}\cdot&-1&\cdot\\\cdot&\cdot&-1\\1&\cdot&\cdot\end{vmatrix}$$

D_4:

$$\mathscr{D}^{T_1}(R_3)=\begin{vmatrix}\cdot&-1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad i_4=\begin{vmatrix}\cdot&-1&\cdot\\-1&\cdot&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad i_1=\begin{vmatrix}\cdot&\cdot&1\\\cdot&-1&\cdot\\1&\cdot&\cdot\end{vmatrix}\quad i_2=\begin{vmatrix}\cdot&\cdot&-1\\\cdot&-1&\cdot\\-1&\cdot&\cdot\end{vmatrix}\quad R_1^3=\begin{vmatrix}1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&-1&\cdot\end{vmatrix}\quad R_1=\begin{vmatrix}1&\cdot&\cdot\\\cdot&\cdot&-1\\\cdot&1&\cdot\end{vmatrix}$$

$$\mathscr{D}^{T_1}(R_3^3)=\begin{vmatrix}\cdot&1&\cdot\\-1&\cdot&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad i_3=\begin{vmatrix}\cdot&1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad R_2=\begin{vmatrix}\cdot&\cdot&1\\\cdot&1&\cdot\\-1&\cdot&\cdot\end{vmatrix}\quad R_2^3=\begin{vmatrix}\cdot&\cdot&-1\\\cdot&1&\cdot\\1&\cdot&\cdot\end{vmatrix}\quad i_6=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&1&\cdot\end{vmatrix}\quad i_5=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&\cdot&-1\\\cdot&-1&\cdot\end{vmatrix}$$

basis:

O	T_1	T_1	T_1
D_4	E	E	A_2
D_2	B_1	B_2	A_2

T_2 *Tensor* yz,xz,xy

$$\mathscr{D}^{T_2}(1)=\begin{vmatrix}1&\cdot&\cdot\\\cdot&1&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad R_1^2=\begin{vmatrix}1&\cdot&\cdot\\\cdot&-1&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad r_1=\begin{vmatrix}\cdot&\cdot&1\\-1&\cdot&\cdot\\\cdot&-1&\cdot\end{vmatrix}\quad r_2=\begin{vmatrix}\cdot&\cdot&-1\\-1&\cdot&\cdot\\\cdot&1&\cdot\end{vmatrix}\quad r_1^2=\begin{vmatrix}\cdot&-1&\cdot\\\cdot&\cdot&-1\\1&\cdot&\cdot\end{vmatrix}\quad r_2^2=\begin{vmatrix}\cdot&-1&\cdot\\\cdot&\cdot&1\\-1&\cdot&\cdot\end{vmatrix}$$

$$\mathscr{D}^{T_2}(R_3^2)=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&-1&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad R_2^2=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&1&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad r_4=\begin{vmatrix}\cdot&\cdot&1\\1&\cdot&\cdot\\\cdot&1&\cdot\end{vmatrix}\quad r_3=\begin{vmatrix}\cdot&\cdot&-1\\1&\cdot&\cdot\\\cdot&-1&\cdot\end{vmatrix}\quad r_3^2=\begin{vmatrix}\cdot&1&\cdot\\\cdot&\cdot&-1\\-1&\cdot&\cdot\end{vmatrix}\quad r_4^2=\begin{vmatrix}\cdot&1&\cdot\\\cdot&\cdot&1\\1&\cdot&\cdot\end{vmatrix}$$

$$\mathscr{D}^{T_2}(R_3)=\begin{vmatrix}\cdot&-1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad i_4=\begin{vmatrix}\cdot&-1&\cdot\\-1&\cdot&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad i_1=\begin{vmatrix}\cdot&\cdot&-1\\\cdot&1&\cdot\\-1&\cdot&\cdot\end{vmatrix}\quad i_2=\begin{vmatrix}\cdot&\cdot&1\\\cdot&1&\cdot\\1&\cdot&\cdot\end{vmatrix}\quad R_1^3=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&-1&\cdot\end{vmatrix}\quad R_1=\begin{vmatrix}-1&\cdot&\cdot\\\cdot&\cdot&-1\\\cdot&1&\cdot\end{vmatrix}$$

$$\mathscr{D}^{T_2}(R_3^3)=\begin{vmatrix}\cdot&1&\cdot\\-1&\cdot&\cdot\\\cdot&\cdot&-1\end{vmatrix}\quad i_3=\begin{vmatrix}\cdot&1&\cdot\\1&\cdot&\cdot\\\cdot&\cdot&1\end{vmatrix}\quad R_2=\begin{vmatrix}\cdot&\cdot&-1\\\cdot&-1&\cdot\\1&\cdot&\cdot\end{vmatrix}\quad R_2^3=\begin{vmatrix}\cdot&\cdot&1\\\cdot&-1&\cdot\\-1&\cdot&\cdot\end{vmatrix}\quad i_6=\begin{vmatrix}1&\cdot&\cdot\\\cdot&\cdot&1\\\cdot&1&\cdot\end{vmatrix}\quad i_5=\begin{vmatrix}1&\cdot&\cdot\\\cdot&\cdot&-1\\\cdot&-1&\cdot\end{vmatrix}$$

basis:

O	T_2	T_2	T_2
D_4	E	E	B_2
D_2	B_1	B_2	A_2

E *Tensor* $x^2+y^2-2z^2$, $(x^2-y^2)\sqrt{3}$

$$\mathscr{D}^{E}(1)\ \begin{vmatrix}1&0\\0&1\end{vmatrix}\quad R_1^2=\begin{vmatrix}1&0\\0&1\end{vmatrix}\quad r_1=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_2=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_1^2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_2^2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}$$

$$\mathscr{D}^{E}(R_3^2)\ \begin{vmatrix}1&0\\0&1\end{vmatrix}\quad R_2^2=\begin{vmatrix}1&0\\0&1\end{vmatrix}\quad r_4=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_3=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_3^2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}\quad r_4^2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{-1}{2}\end{vmatrix}$$

$$\mathscr{D}^{E}(R_3)\ \begin{vmatrix}1&0\\0&-1\end{vmatrix}\quad i_4=\begin{vmatrix}1&0\\0&-1\end{vmatrix}\quad i_1=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad i_2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad R_1^3=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad R_1=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{1}{2}\end{vmatrix}$$

$$\mathscr{D}^{E}(R_3^3)\ \begin{vmatrix}1&0\\0&-1\end{vmatrix}\quad i_3=\begin{vmatrix}1&0\\0&-1\end{vmatrix}\quad R_2=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad R_2^3=\begin{vmatrix}\frac{-1}{2}&\frac{\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad i_6=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{\sqrt3}{2}&\frac{1}{2}\end{vmatrix}\quad i_5=\begin{vmatrix}\frac{-1}{2}&\frac{-\sqrt3}{2}\\\frac{-\sqrt3}{2}&\frac{1}{2}\end{vmatrix}$$

basis:

O	E	E
D_4	A_1	B_1
D_2	A_1	A_1

AMOPclass17 p.85.
PSDS TablesF pdf p.12.

O: $\chi_{\mathbf{g}}^{\mu}$	g=1	$\mathbf{r}_{1-4}$ $\tilde{\mathbf{r}}_{1-4}$	ρ_{xyz}	$\mathbf{R}_{xyz}$ $\tilde{\mathbf{R}}_{xyz}$	$\mathbf{i}_{1-6}$
$\mu=A_1$	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

AMOP reference links on pages 2-4

4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Molecular rovibrational spectra : O_h symmetry, SF_6 and UF_6 examples

SF_6 has octahedral ($O_h \supset O \supset C_{4v}$ or C_{3v}) symmetry

SF_6 octahedral ($O_h \supset C_{4v}$) Cartesian coordination

SF_6 octahedral ($O_h \supset C_{4v}$) symmetry coordination

- SF_6 octahedral ($O_h \supset C_{4v}$) mode labeling

Ireps for $O \supset D_4 \supset D_2$ subgroup chain and coset factored projectors

- Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors
- Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

- Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics
- Modes and energy level diagrams: SF_6, UF_6, etc.
  - SF_6, overtones and harmonics
- Coriolis orbits of T_{1u} modes ν_3 ($947 cm^{-1}$) and ν_4 ($630 cm^{-1}$) of SF_6

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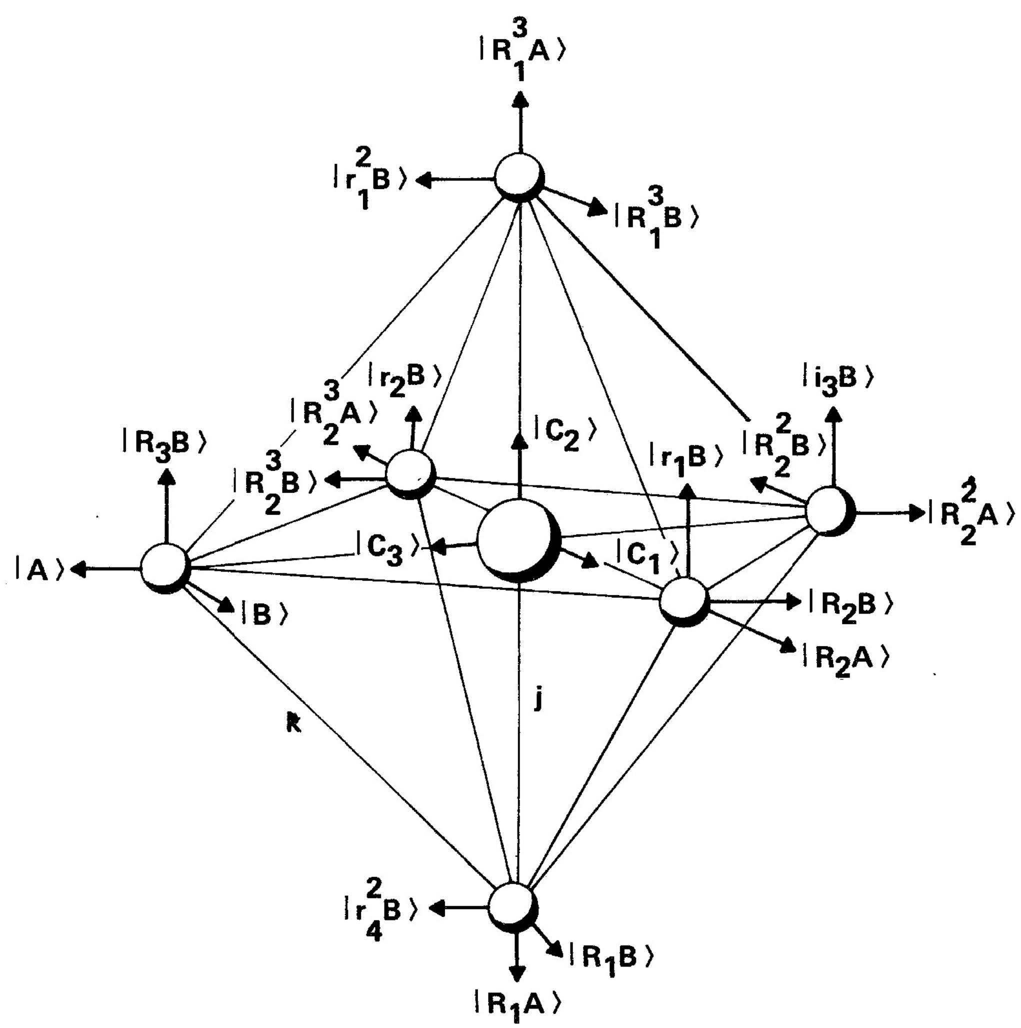
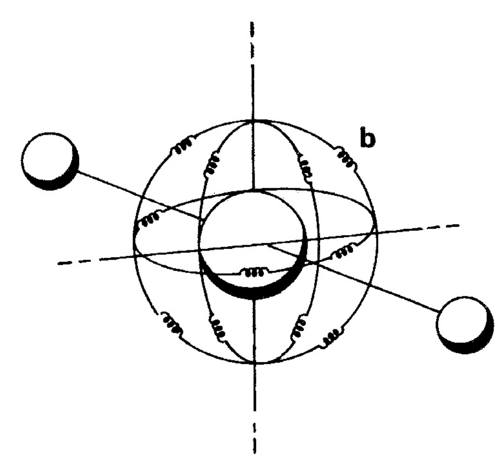
- Nomogram of T_{1u} SF_6 ν_4 P(88) fine, superfine, and hyperfine structure

Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors

	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$



Model of "covalence"
or bending force

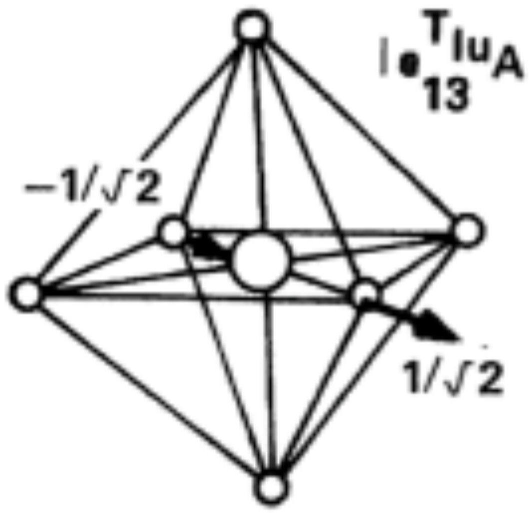


Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors

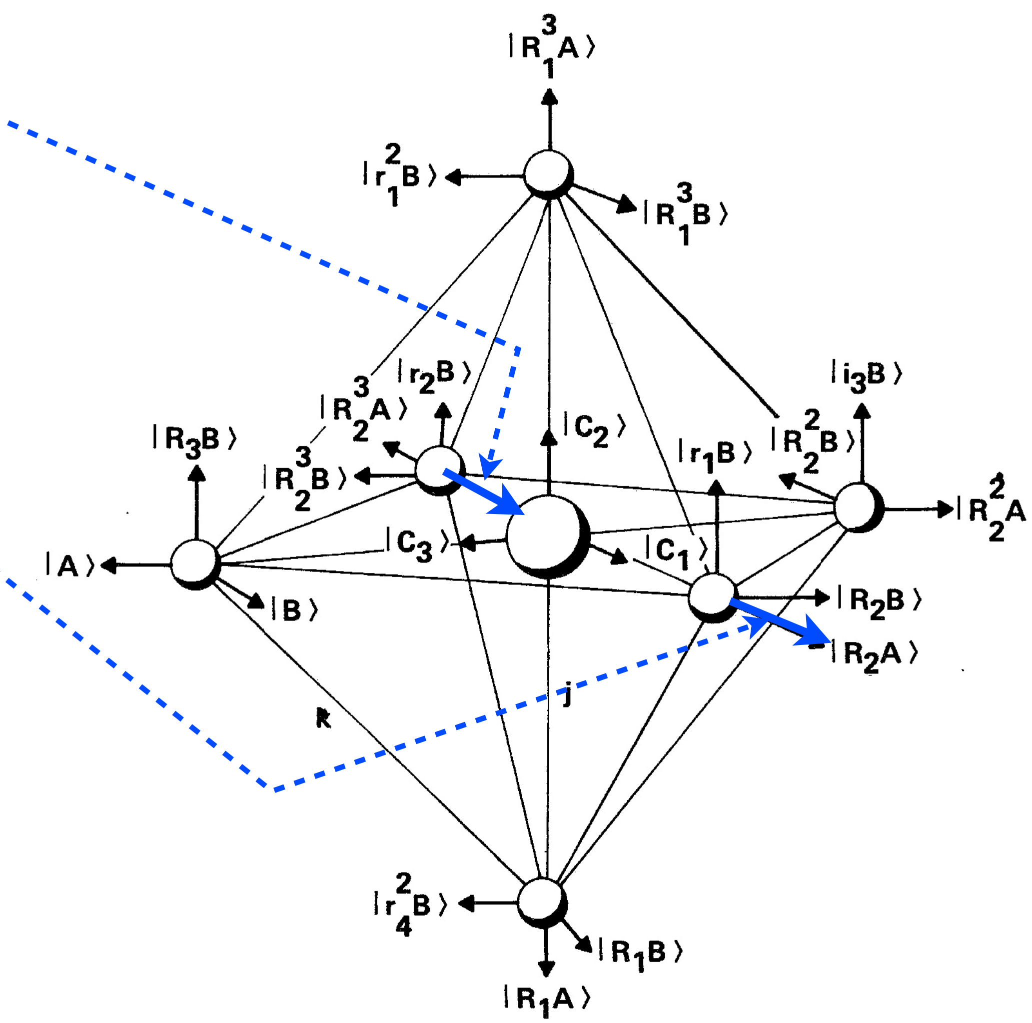
PSDS Ch.4 p.67.

x-translation in A space

$e_{11}^{T_{1u}} A$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
				$\frac{1}{\sqrt{2}}$		$\frac{-1}{\sqrt{2}}$															



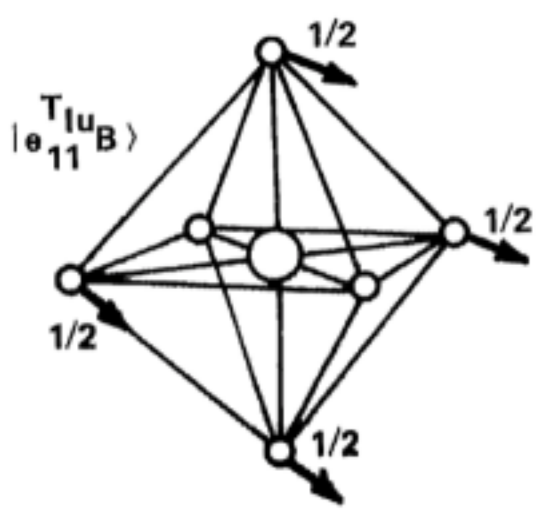
x-translation
momentum=$m\cdot\sqrt{2}$



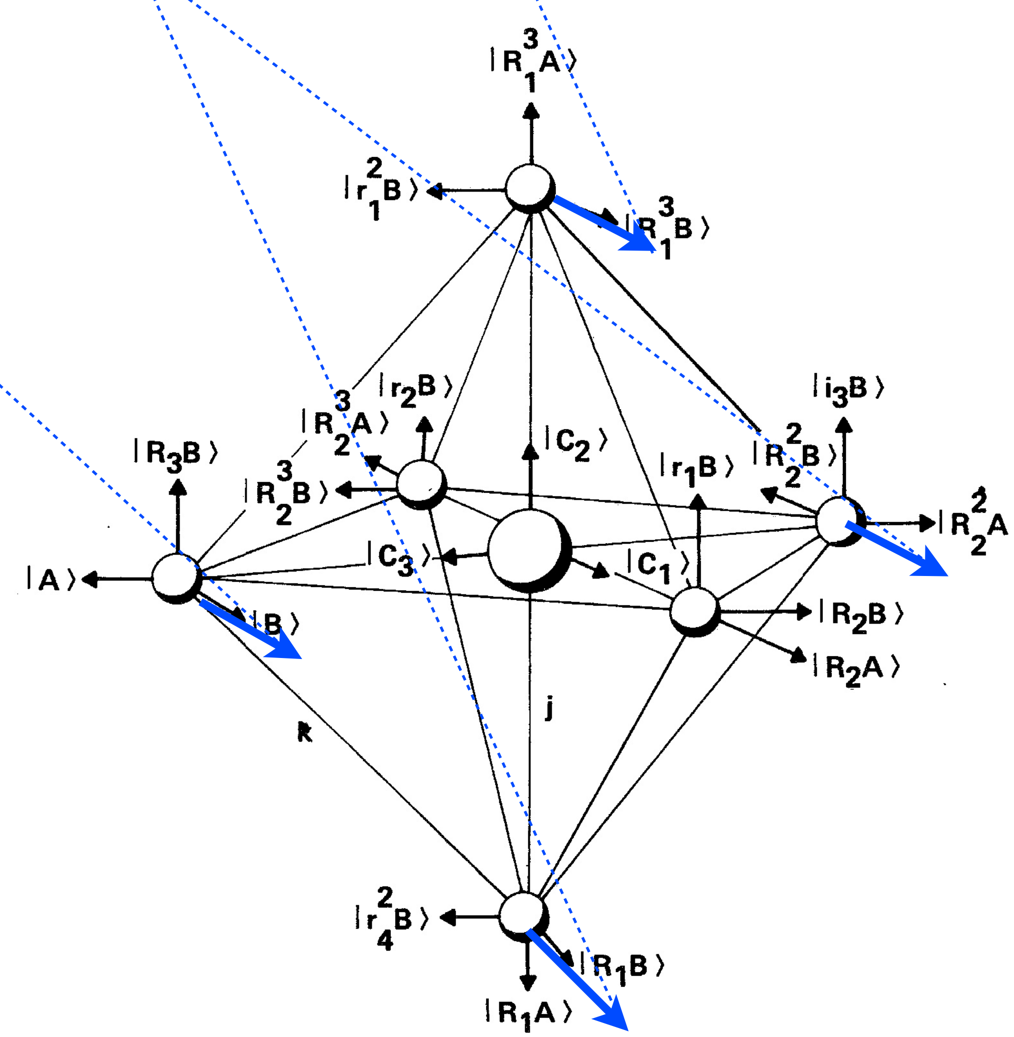
Sorting |T1u⟩A, |T1u⟩B, and |T1u⟩C mode vectors

x-translation in B space

$e_{11}^{T_{1u}}B$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
							$\frac{1}{2}$					$-\frac{1}{2}$	$\frac{1}{2}$			$\frac{1}{2}$					



x-translation
momentum=$m\cdot 2$

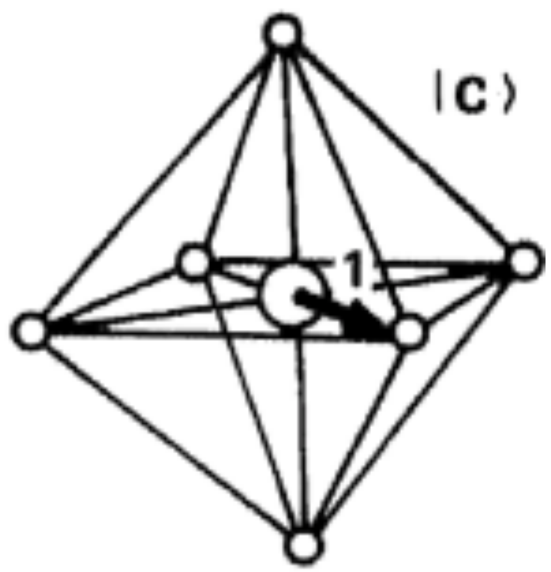


Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors

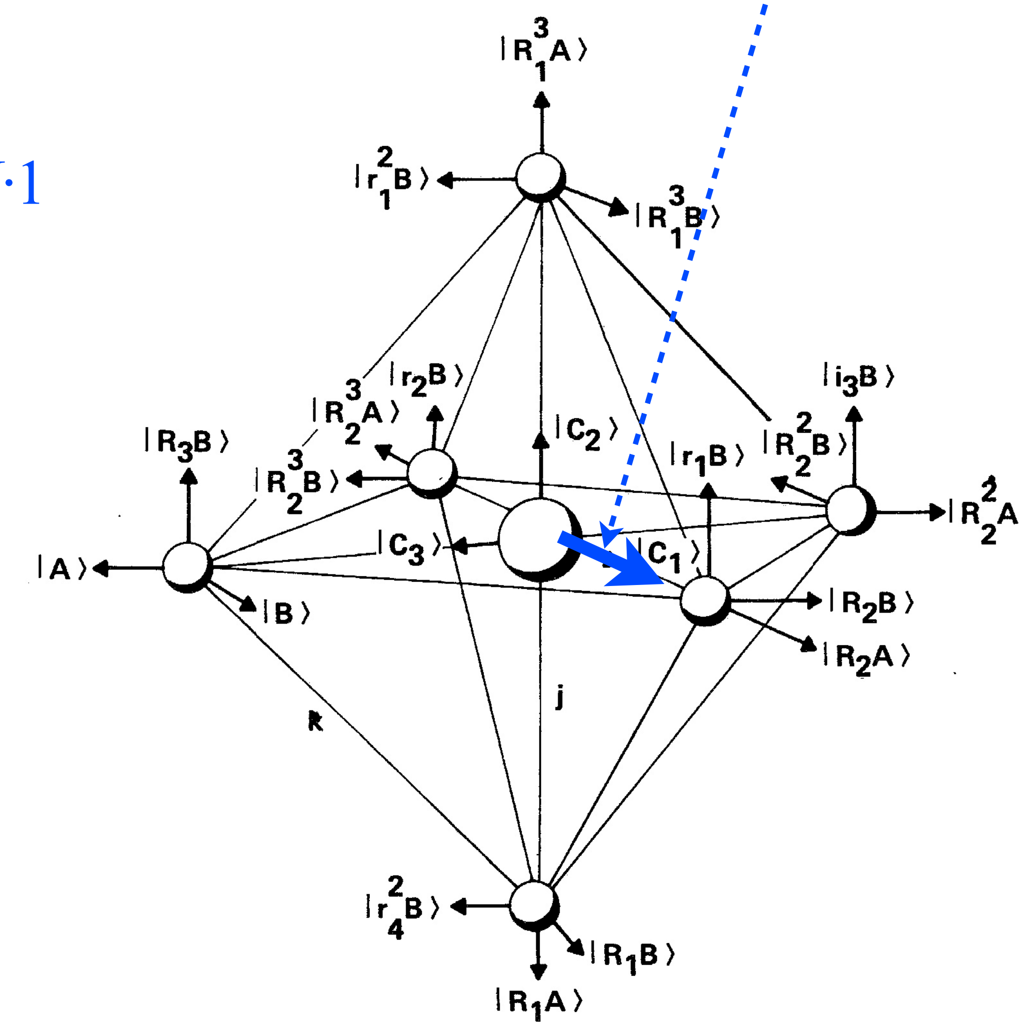
PSDS Ch.4 p.67.

x-translation in C space

$e^{T_{1u}}_{11}C$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
																			1		



x-translation
momentum=$M\cdot 1$



AMOP reference links on pages 2-4

4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

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Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum

x-translation in A space

PSDS Ch.4 p.67.

$e_{11}^{T_{1u}}A$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
				$\frac{1}{\sqrt{2}}$		$\frac{-1}{\sqrt{2}}$															

x-translation in B space

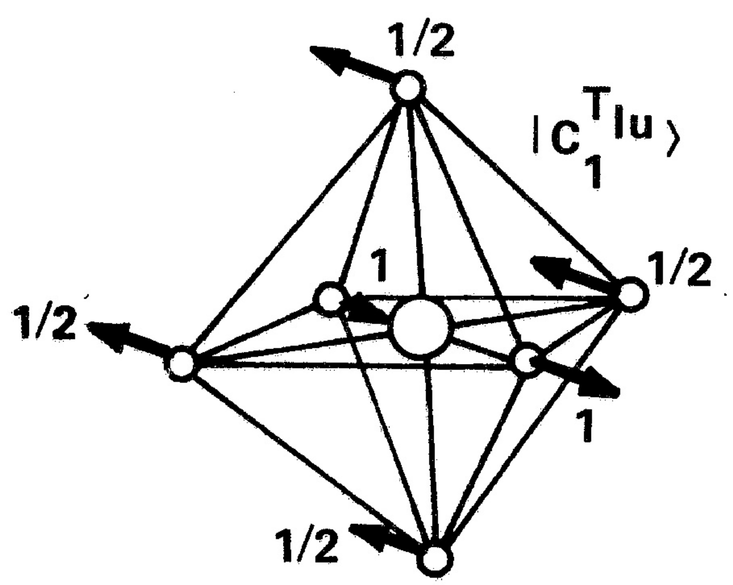
$e_{11}^{T_{1u}}B$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
							$\frac{1}{2}$					$-\frac{1}{2}$	$\frac{1}{2}$			$\frac{1}{2}$					

x-translation in C space

$e_{11}^{T_{1u}}C$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
																			1		

Combining A and B space to zero momentum

$$\left|c_{j1}^{T_{1u}}0\right\rangle = \sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle - \left|e_{j1}^{T_{1u}}B\right\rangle = 2\mathbf{P}_{j3}^{T_{1u}}|A\rangle - 2\mathbf{P}_{j1}^{T_{1u}}|B\rangle$$



Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum

x-translation in A space

PSDS Ch.4 p.67.

$e_{11}^{T_{1u}}A$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
				$\frac{1}{\sqrt{2}}$		$\frac{-1}{\sqrt{2}}$															

x-translation in B space

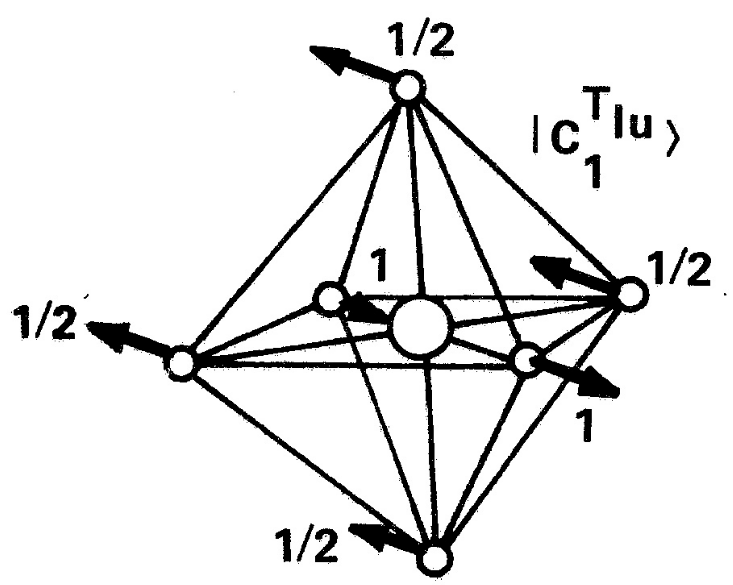
$e_{11}^{T_{1u}}B$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
							$\frac{1}{2}$					$-\frac{1}{2}$	$\frac{1}{2}$			$\frac{1}{2}$					

x-translation in C space

$e_{11}^{T_{1u}}C$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
																			1		

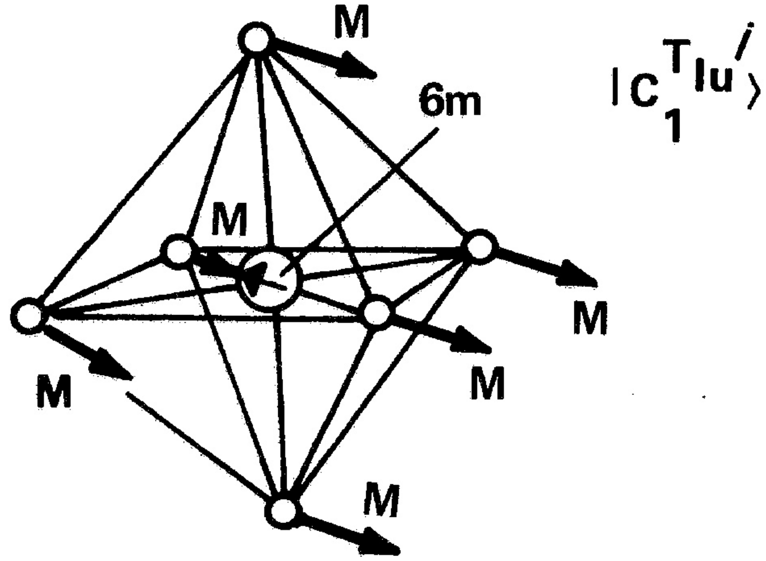
Combining A and B space to zero momentum

$$\left|c_{j1}^{T_{1u}}0\right\rangle = \sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle - \left|e_{j1}^{T_{1u}}B\right\rangle = 2\mathbf{P}_{j3}^{T_{1u}}|A\rangle - 2\mathbf{P}_{j1}^{T_{1u}}|B\rangle$$



Combining A, B and C space to zero momentum

$$\left|c_{j1}^{T_{1u}'}0\right\rangle = M\sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle + 2M\left|e_{j1}^{T_{1u}}B\right\rangle - 6m\left|C_j\right\rangle$$



Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum

x-translation in A space

PSDS Ch.4 p.67.

$e_{11}^{T_{1u}}A$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
				$\frac{1}{\sqrt{2}}$		$\frac{-1}{\sqrt{2}}$															

x-translation in B space

$e_{11}^{T_{1u}}B$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
							$\frac{1}{2}$					$-\frac{1}{2}$	$\frac{1}{2}$			$\frac{1}{2}$					

x-translation in C space

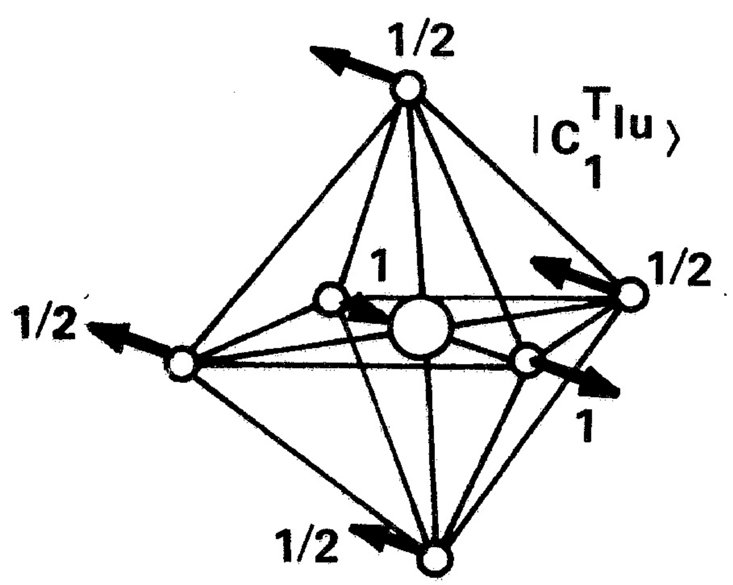
$e_{11}^{T_{1u}}C$	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
																			1		

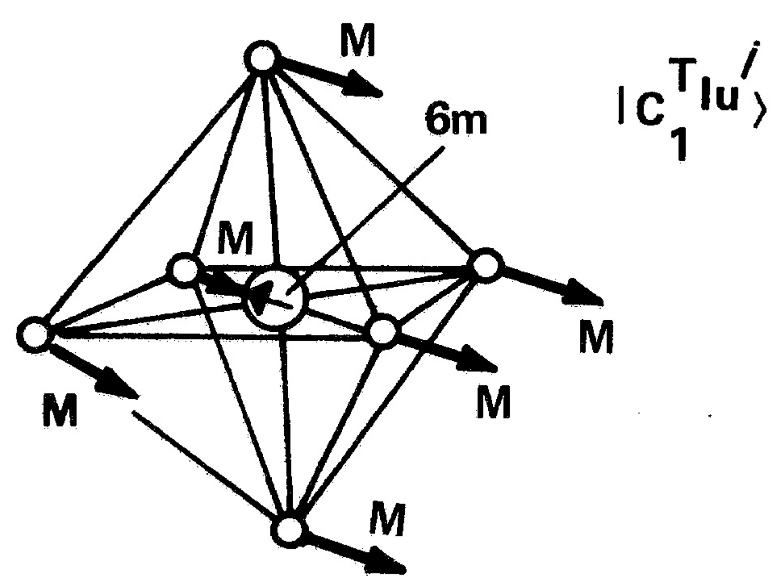
Combining A and B space to zero momentum

$$\left|c_{j1}^{T_{1u}}0\right\rangle = \sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle - \left|e_{j1}^{T_{1u}}B\right\rangle = 2\mathbf{P}_{j3}^{T_{1u}}\left|A\right\rangle - 2\mathbf{P}_{j1}^{T_{1u}}\left|B\right\rangle$$

Combining A, B and C space to zero momentum

$$\left|c_{j1}^{T_{1u}'}0\right\rangle = M\sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle + 2M\left|e_{j1}^{T_{1u}}B\right\rangle - 6m\left|C_j\right\rangle$$





T_{1u} *translation (discarded)*

A third state is one of rigid translation

$$\left|c_{j1}^{T_{1u}}rigid\right\rangle = \sqrt{2}\left|e_{j3}^{T_{1u}}A\right\rangle + 2\left|e_{j1}^{T_{1u}}B\right\rangle + \left|C_j\right\rangle$$

AMOP reference links on pages 2-4

4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

William G. Harter - University of Arkansas

Molecular rovibrational spectra : O_h symmetry, SF_6 and UF_6 examples

SF_6 has octahedral ($O_h \supset O \supset C_{4v}$ or C_{3v}) symmetry

SF_6 octahedral ($O_h \supset C_{4v}$) Cartesian coordination

SF_6 octahedral ($O_h \supset C_{4v}$) symmetry coordination

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Ireps for $O \supset D_4 \supset D_2$ subgroup chain and coset factored projectors

Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors

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➡ Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics

Modes and energy level diagrams: SF_6, UF_6, etc.

SF_6, overtones and harmonics

Coriolis orbits of T_{1u} modes ν_3 ($947 cm^{-1}$) and ν_4 ($630 cm^{-1}$) of SF_6

Graphical interpretation of Coriolis T_{1u} effects in ν_4 ($630 cm^{-1}$)

Rovibronic Nomogram of Coriolis T_{1u} effects

Tensor centrifugal and Coriolis T_{1u} effects in ν_4 P(88) fine structure

Nomogram of T_{1u} SF_6 ν_4 P(88) fine, superfine, and hyperfine structure

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

Having non-orthonormal states involves non-Hermitian mass and force operator equations

Newton-like mode equations: $\mathbf{m}\left|\ddot{x}\right\rangle = -\mathbf{F}\left|x\right\rangle$ give $(\text{frequency})^2$ eigenvalues: $\left(\omega^{(\alpha)}\right)^2\left|x^{(\alpha)}\right\rangle = \mathbf{F}\bullet\mathbf{m}^{-1}\left|x^{(\alpha)}\right\rangle$

$\langle F\rangle =$

	$\lvert 1\rangle_A$	$\lvert R_1^2\rangle$	$\lvert R_1\rangle$	$\lvert R_2\rangle$	$\lvert R_1^3\rangle$	$\lvert R_2^3\rangle$	$\lvert 1\rangle_B$	$\lvert r_1\rangle$	$\lvert r_2\rangle$	$\lvert r_1^2\rangle$	$\lvert r_4^2\rangle$	$\lvert R_2^2\rangle$	$\lvert R_1\rangle$	$\lvert R_2\rangle$	$\lvert R_3\rangle$	$\lvert R_1^3\rangle$	$\lvert R_2^3\rangle$	$\lvert i_3\rangle$	$\lvert 1\rangle_C$	$\lvert 2\rangle$	$\lvert 3\rangle$
$\langle A\rvert$	$2k+j$	0	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	0	0	0	$\frac{-k}{2}$	$\frac{-k}{2}$	0	0	$\frac{k}{2}$	0	0	$\frac{-k}{2}$	0	0	0	$-j$
$\langle B\rvert$							$k+b$	0	0	0	0	0	0	$\frac{-(k+b)}{2}$	0	0	$\frac{-(k+b)}{2}$	0	$\frac{-b}{2}$	0	0
$\langle C\rvert$																			$2(j+b)$	0	0

$\langle m\rangle =$

	$\lvert 1\rangle_A$	$\lvert R_1^2\rangle$	$\lvert R_1\rangle$	$\lvert R_2\rangle$	$\lvert R_1^3\rangle$	$\lvert R_2^3\rangle$	$\lvert 1\rangle_B$	$\lvert r_1\rangle$	$\lvert r_2\rangle$	$\lvert r_1^2\rangle$	$\lvert r_4^2\rangle$	$\lvert R_2^2\rangle$	$\lvert R_1\rangle$	$\lvert R_2\rangle$	$\lvert R_3\rangle$	$\lvert R_1^3\rangle$	$\lvert R_2^3\rangle$	$\lvert i_3\rangle$	$\lvert 1\rangle_C$	$\lvert 2\rangle$	$\lvert 3\rangle$
$\langle A\rvert$	m	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\langle B\rvert$							m	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\langle C\rvert$																			M	0	0

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

PSDS Ch.4 p.72.

Having non-orthonormal states involves non-Hermitian mass and force operator equations

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$\langle F\rangle =$

	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
$\langle A\|$	$2k+j$	0	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	0	0	0	$\frac{-k}{2}$	$\frac{-k}{2}$	0	0	$\frac{k}{2}$	0	0	$\frac{-k}{2}$	0	0	0	$-j$
$\langle B\|$							$k+b$	0	0	0	0	0	0	$\frac{-(k+b)}{2}$	0	0	$\frac{-(k+b)}{2}$	0	$\frac{-b}{2}$	0	0
$\langle C\|$																			$2(j+b)$	0	0

For A and B spaces the eigenvalues are simple projector sums

$$\left(\omega^{A_{1g}}\right)^2 = \frac{1}{m}\sum_{\mathbf{g}_\ell}\langle A|\mathbf{F}|\mathbf{g}_\ell A\rangle D^{A_{1g}}(\mathbf{g}_\ell) = [(4k+j)]/m$$

$$\left(\omega^{E_g}\right)^2 = \frac{1}{m}\sum_{\mathbf{g}_\ell}\langle A|\mathbf{F}|\mathbf{g}_\ell A\rangle D^{E_g}(\mathbf{g}_\ell) = [(k+j)]/m$$

$$\left(\omega^{T_{2u}}\right)^2 = \frac{1}{m}\sum_{\mathbf{g}_\ell}\langle B|\mathbf{F}|\mathbf{g}_\ell B\rangle D_{11}^{T_{2u}}(\mathbf{g}_\ell) = \left[(k+b)D_{11}^{T_{2u}}(1) - \frac{k+b}{2}\left(D_{11}^{T_{2u}}(\mathbf{R}_2) + D_{11}^{T_{2u}}(\mathbf{R}_2^3)\right)\right]/m = \frac{k+b}{m}$$

$$\left(\omega^{T_{2g}}\right)^2 = \frac{1}{m}\sum_{\mathbf{g}_\ell}\langle B|\mathbf{F}|\mathbf{g}_\ell B\rangle D_{22}^{T_{2g}}(\mathbf{g}_\ell) = \left[(k+b)D_{22}^{T_{2g}}(1) - \frac{k+b}{2}\left(D_{22}^{T_{2g}}(\mathbf{R}_2) + D_{22}^{T_{2g}}(\mathbf{R}_2^3)\right)\right]/m = 2\frac{k+b}{m}$$

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

T_{1u} vector symmetry involves A, B and C space 2-by-2 matrices of **Q=F** and **Q=m**.

in zero-p basis: $\left|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = \sqrt{2}\left|e^{T_{1u}}_{j3}A\right\rangle - \left|e^{T_{1u}}_{j1}B\right\rangle = 2\mathbf{P}^{T_{1u}}_{j3}\left|A\right\rangle - 2\mathbf{P}^{T_{1u}}_{j1}\left|B\right\rangle$ and: $\left|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = M\sqrt{2}\left|e^{T_{1u}}_{j3}A\right\rangle + 2M\left|e^{T_{1u}}_{j1}B\right\rangle - 6m\left|C_j\right\rangle$

11-Matrix $\left\langle T_{1u}\right|Q\left|T_{1u}\right\rangle$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\right|\mathbf{Q}\left|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = \left(2\left\langle A\right|\mathbf{P}^{T_{1u}}_{3j} - 2\left\langle B\right|\mathbf{P}^{T_{1u}}_{1j}\right)\mathbf{Q}\left(2\mathbf{P}^{T_{1u}}_{j3}\left|A\right\rangle - 2\mathbf{P}^{T_{1u}}_{j1}\left|B\right\rangle\right)$$

$$= 4\left\langle A\right|\mathbf{P}^{T_{1u}}_{33}\mathbf{Q}\left|A\right\rangle - 4\left\langle A\right|\mathbf{P}^{T_{1u}}_{31}\mathbf{Q}\left|B\right\rangle - 4\left\langle B\right|\mathbf{P}^{T_{1u}}_{13}\mathbf{Q}\left|A\right\rangle - 4\left\langle B\right|\mathbf{P}^{T_{1u}}_{11}\mathbf{Q}\left|B\right\rangle = 2Q_{AA} - \sqrt{2}Q_{AB} + 2Q_{BB} - \sqrt{2}Q_{BA}$$

Each term reduces to group coset leader sums:

$$Q_{AA} = \sum_{\mathbf{g}_\ell}\left\langle A\right|\mathbf{Q}\left|\mathbf{g}_\ell A\right\rangle D^{T_{1u}}_{33}(\mathbf{g}_\ell), \qquad Q_{AB} = \tfrac{1}{\sqrt{2}}\sum_{\mathbf{g}_\ell}\left\langle A\right|\mathbf{Q}\left|\mathbf{g}_\ell A\right\rangle D^{T_{1u}}_{31}(\mathbf{g}_\ell) = Q_{BA}, \qquad Q_{BB} = \sum_{\mathbf{g}_\ell}\left\langle B\right|\mathbf{Q}\left|\mathbf{g}_\ell B\right\rangle D^{T_{1u}}_{11}(\mathbf{g}_\ell)$$

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

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11-Matrix $\langle T_{1u}|Q|T_{1u}\rangle$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\right|\mathbf{Q}\left|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = \left(2\langle A|\mathbf{P}^{T_{1u}}_{3j} - 2\langle B|\mathbf{P}^{T_{1u}}_{1j}\right)\mathbf{Q}\left(2\mathbf{P}^{T_{1u}}_{j3}|A\rangle - 2\mathbf{P}^{T_{1u}}_{j1}|B\rangle\right)$$

$$= 4\langle A|\mathbf{P}^{T_{1u}}_{33}\mathbf{Q}|A\rangle \;-\; 4\langle A|\mathbf{P}^{T_{1u}}_{31}\mathbf{Q}|B\rangle \;-\; 4\langle B|\mathbf{P}^{T_{1u}}_{13}\mathbf{Q}|A\rangle \;-\; 4\langle B|\mathbf{P}^{T_{1u}}_{11}\mathbf{Q}|B\rangle \;=\; 2Q_{AA} - \sqrt{2}Q_{AB} + 2Q_{BB} - \sqrt{2}Q_{BA}$$

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For **Q=F**: $\begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB} \end{pmatrix} = \begin{pmatrix} 2k+j & -\sqrt{2}k \\ -\sqrt{2}k & k+b \end{pmatrix}$

For **Q=m**: $\begin{pmatrix} m_{AA} & m_{AB} \\ m_{BA} & m_{BB} \end{pmatrix} = \begin{pmatrix} m & 0 \\ 0 & m \end{pmatrix}$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\right|\mathbf{F}\left|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = 2F_{AA} - \sqrt{2}F_{AB} + 2F_{BB} - \sqrt{2}F_{BA} = 9k + 2j + b$$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\right|\mathbf{m}\left|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = 2m_{AA} - \sqrt{2}m_{AB} + 2m_{BB} - \sqrt{2}m_{BA} = 3m$$

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

PSDS Ch.4 p.72.

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11-Matrix $\langle T_{1u}|Q|T_{1u}\rangle$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{Q}\middle|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = \left(2\langle A|\mathbf{P}^{T_{1u}}_{3j} - 2\langle B|\mathbf{P}^{T_{1u}}_{1j}\right)\mathbf{Q}\left(2\mathbf{P}^{T_{1u}}_{j3}|A\rangle - 2\mathbf{P}^{T_{1u}}_{j1}|B\rangle\right)$$

$$= 4\langle A|\mathbf{P}^{T_{1u}}_{33}\mathbf{Q}|A\rangle \text{ - } 4\langle A|\mathbf{P}^{T_{1u}}_{31}\mathbf{Q}|B\rangle \text{ - } 4\langle B|\mathbf{P}^{T_{1u}}_{13}\mathbf{Q}|A\rangle \text{ - } 4\langle B|\mathbf{P}^{T_{1u}}_{11}\mathbf{Q}|B\rangle = 2Q_{AA} - \sqrt{2}Q_{AB} + 2Q_{BB} - \sqrt{2}Q_{BA}$$

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For **Q=F**: $\begin{pmatrix} F_{AA} & F_{AB} \\ F_{BA} & F_{BB}\end{pmatrix} = \begin{pmatrix} 2k+j & -\sqrt{2}k \\ -\sqrt{2}k & k+b\end{pmatrix}$

For **Q=m**: $\begin{pmatrix} m_{AA} & m_{AB} \\ m_{BA} & m_{BB}\end{pmatrix} = \begin{pmatrix} m & 0 \\ 0 & m\end{pmatrix}$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{F}\middle|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = 2F_{AA} - \sqrt{2}F_{AB} + 2F_{BB} - \sqrt{2}F_{BA} = 9k + 2j + b$$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{m}\middle|c^{T_{1u}}_{j1\text{-}3}0\right\rangle = 2m_{AA} - \sqrt{2}m_{AB} + 2m_{BB} - \sqrt{2}m_{BA} = 3m$$

12-Matrix $\langle T_{1u}|Q|T'_{1u}\rangle$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{Q}\middle|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = 2MQ_{AA} + 2\sqrt{2}MQ_{AB} - \sqrt{2}MQ_{BA} - 2MQ_{BB} - \sqrt{2}Q_{BA} - 12m\left(\langle A|\mathbf{Q}|C\rangle - \langle B|\mathbf{Q}|C\rangle\right)$$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{F}\middle|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = 2(j-b)(M+6m)$$

$$\left\langle c^{T_{1u}}_{j1\text{-}3}0\middle|\mathbf{m}\middle|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = 0$$

22-Matrix $\langle T'_{1u}|Q|T'_{1u}\rangle$

$$\left\langle c^{T'_{1u}}_{j1\text{-}3}0\middle|\mathbf{F}\middle|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = (2j+4b)(M+6m)^2$$

$$\left\langle c^{T'_{1u}}_{j1\text{-}3}0\middle|\mathbf{m}\middle|c^{T'_{1u}}_{j1\text{-}3}0\right\rangle = 6mM(M+6m)$$

AMOP reference links on pages 2-4

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Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

- ➡ Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics
- Modes and energy level diagrams: SF_6, UF_6, etc.
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Graphical interpretation of Coriolis T_{1u} effects in ν_4 (630cm^{-1})

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Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics

$$\langle \mathbf{a} \rangle = \langle \mathbf{m} \rangle^{-1} \langle \mathbf{F} \rangle = \begin{pmatrix} \left\langle c^{T_{1u}}_{j1\text{-}3} 0 \middle| \mathbf{a} \middle| c^{T_{1u}}_{j1\text{-}3} 0 \right\rangle & \left\langle c^{T_{1u}}_{j1\text{-}3} 0 \middle| \mathbf{a} \middle| c^{T'_{1u}}_{j1\text{-}3} 0 \right\rangle = \\ \left\langle c^{T'_{1u}}_{j1\text{-}3} 0 \middle| \mathbf{a} \middle| c^{T_{1u}}_{j1\text{-}3} 0 \right\rangle & \left\langle c^{T'_{1u}}_{j1\text{-}3} 0 \middle| \mathbf{a} \middle| c^{T'_{1u}}_{j1\text{-}3} 0 \right\rangle \end{pmatrix} = \begin{pmatrix} \frac{9k+2j+b}{3m} & \frac{2(j-b)(M+6m)}{3m} \\ \frac{(j-b)}{3mM} & \frac{(2j+4b)(M+6m)}{3mM} \end{pmatrix}$$

Secular equation gives square-frequency eigenvalues

Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics

$$\langle \mathbf{a} \rangle = \langle \mathbf{m} \rangle^{-1} \langle \mathbf{F} \rangle = \begin{pmatrix} \left\langle c_{j1\text{-}3}^{T_{1u}} 0 \middle| \mathbf{a} \middle| c_{j1\text{-}3}^{T_{1u}} 0 \right\rangle & \left\langle c_{j1\text{-}3}^{T_{1u}} 0 \middle| \mathbf{a} \middle| c_{j1\text{-}3}^{T'_{1u}} 0 \right\rangle = \\ \left\langle c_{j1\text{-}3}^{T'_{1u}} 0 \middle| \mathbf{a} \middle| c_{j1\text{-}3}^{T_{1u}} 0 \right\rangle & \left\langle c_{j1\text{-}3}^{T'_{1u}} 0 \middle| \mathbf{a} \middle| c_{j1\text{-}3}^{T'_{1u}} 0 \right\rangle \end{pmatrix} = \begin{pmatrix} \frac{9k+2j+b}{3m} & \frac{2(j-b)(M+6m)}{3m} \\ \frac{(j-b)}{3mM} & \frac{(2j+4b)(M+6m)}{3mM} \end{pmatrix}$$

Secular equation gives square-frequency eigenvalues

$\lambda^2 - S\lambda + P = 0$ gives eigenvalues $\lambda_e = \left(\omega_e^{T_{1u}}\right)^2$ in terms of their

Sum $S = \lambda_+ + \lambda_- = \frac{3k+j+b}{m} + \frac{2j+4b}{M}$ and their Product $P = \lambda_+ \lambda_- = \frac{(kj+2kb+jb)(M+6m)}{m^2 M}$

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$$\omega_\pm^{T_{1u}} = \sqrt{\frac{S \pm \sqrt{S^2 - 4P}}{2}}$$

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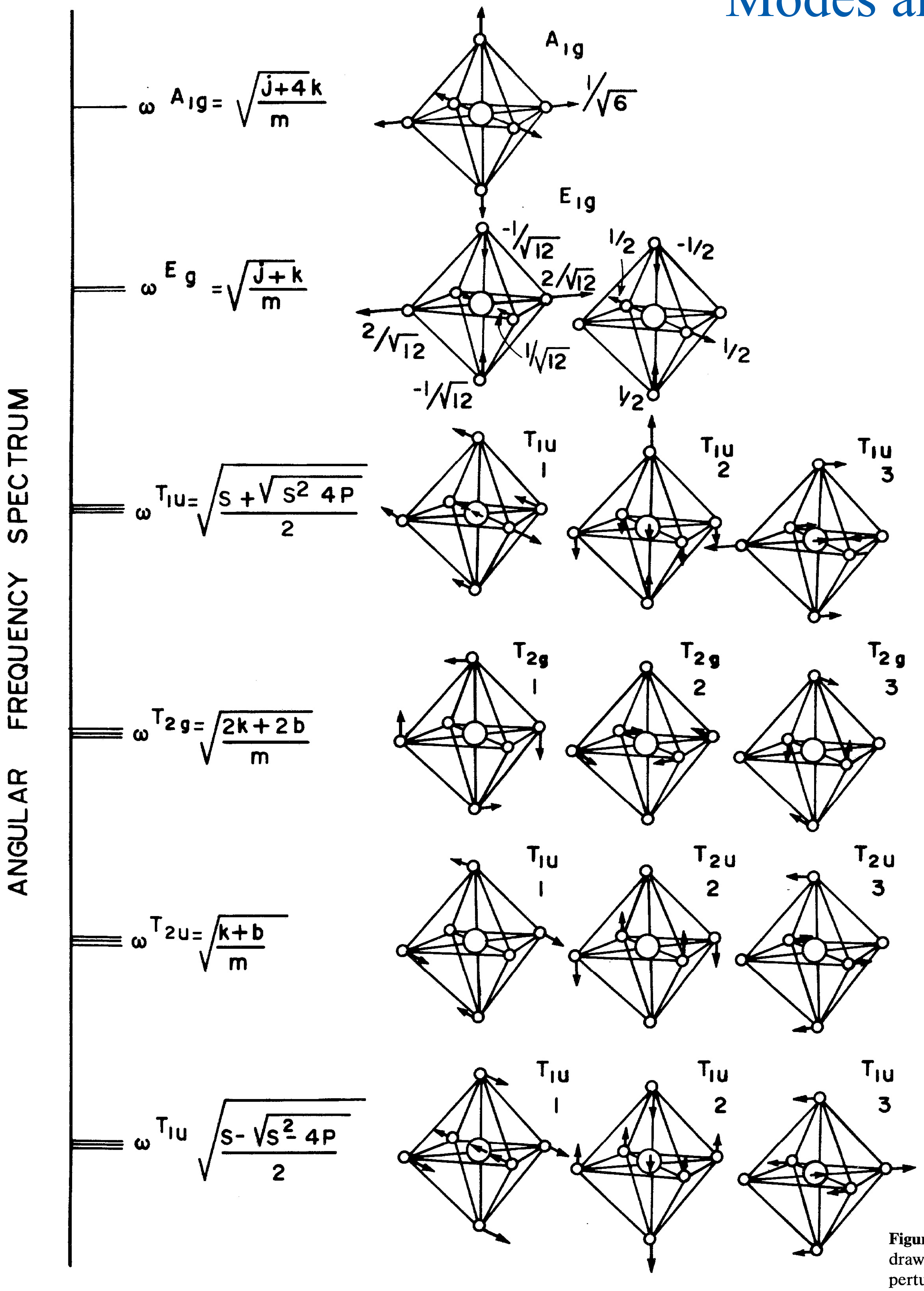

Figure 4.4.3 Hexafluoride vibrational modes and spectrum. T_{1u} modes are not drawn precisely, since their form depends upon the choice of constants and rotational perturbations. (See Figure 4.4.7.)

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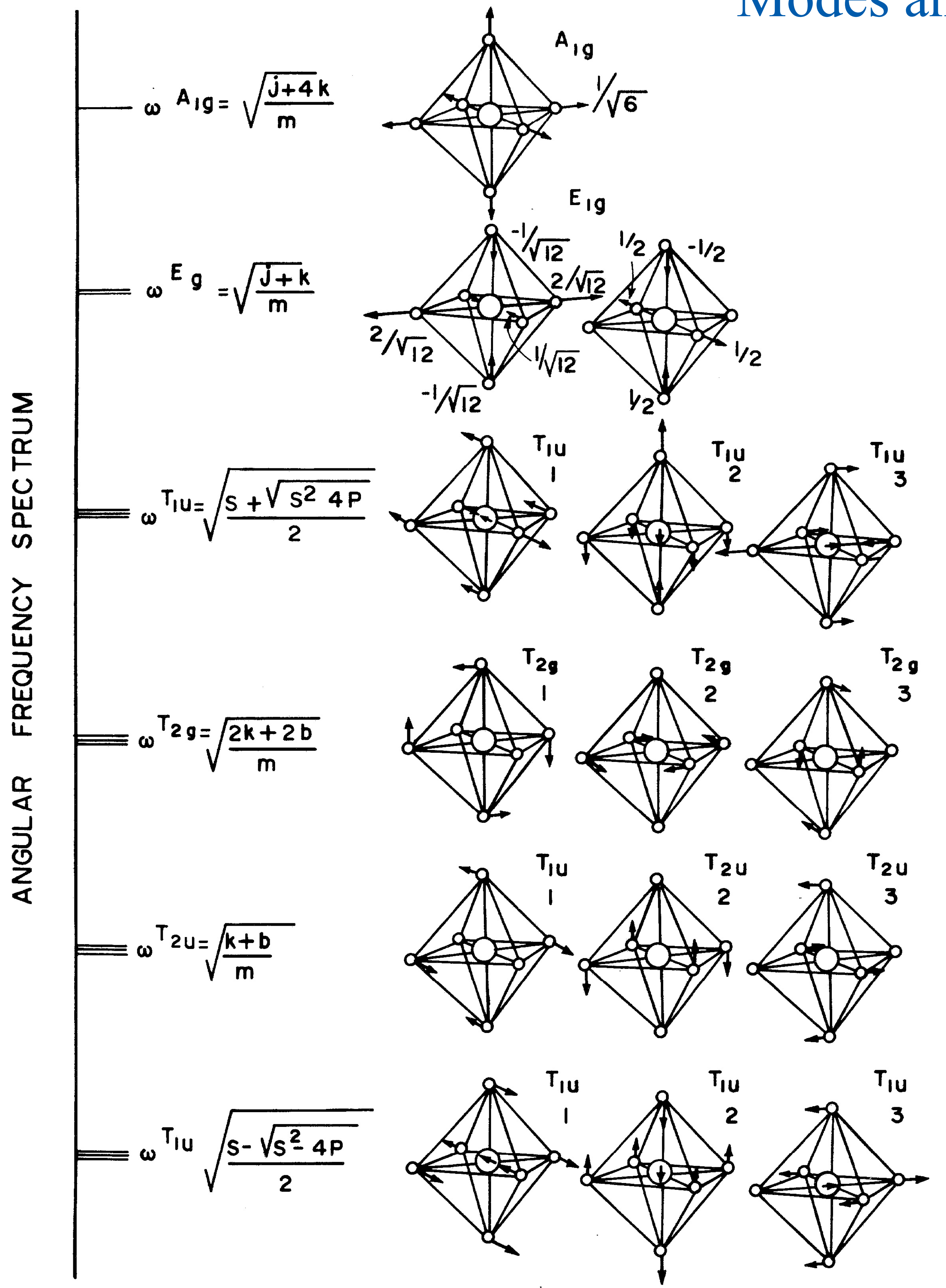

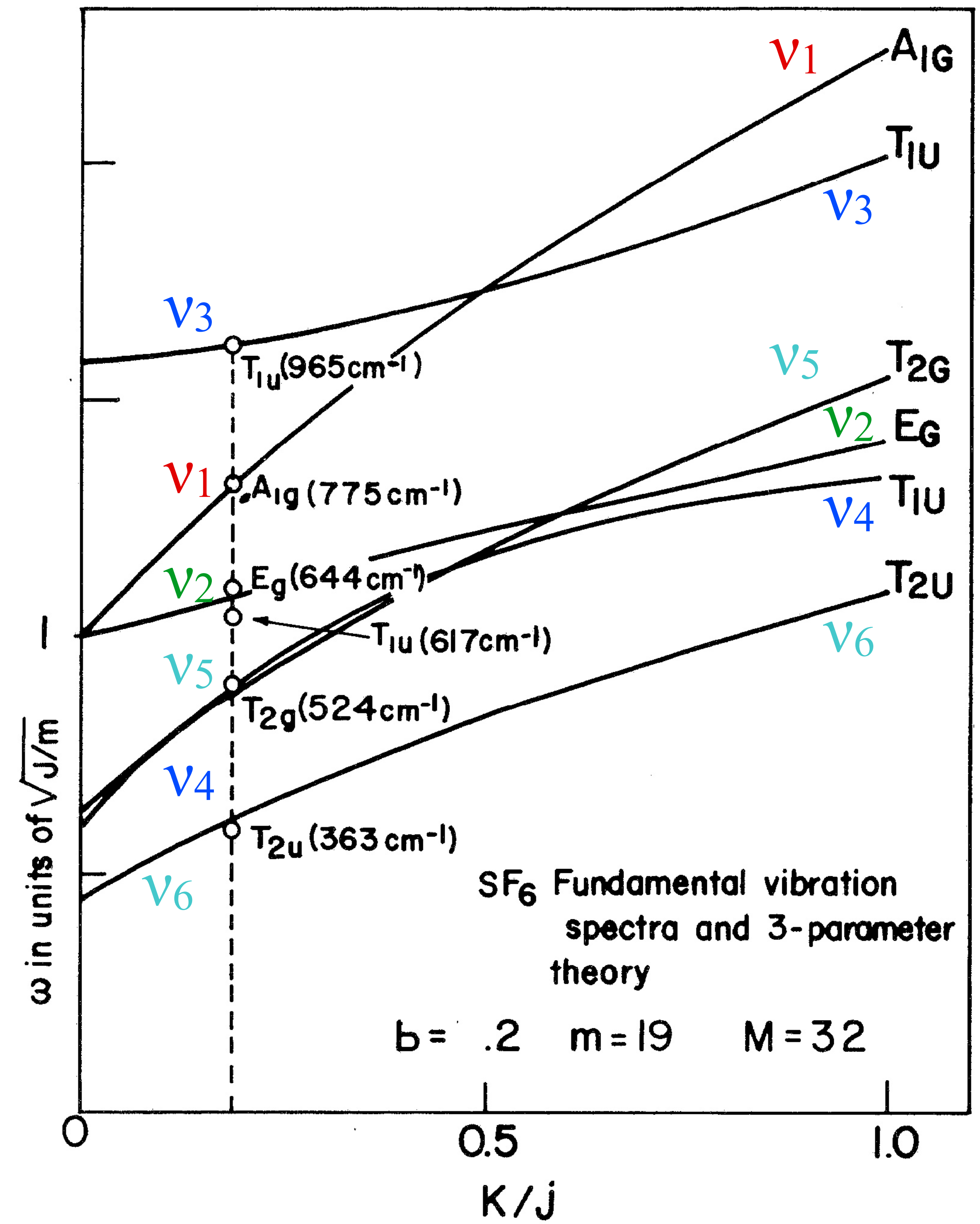

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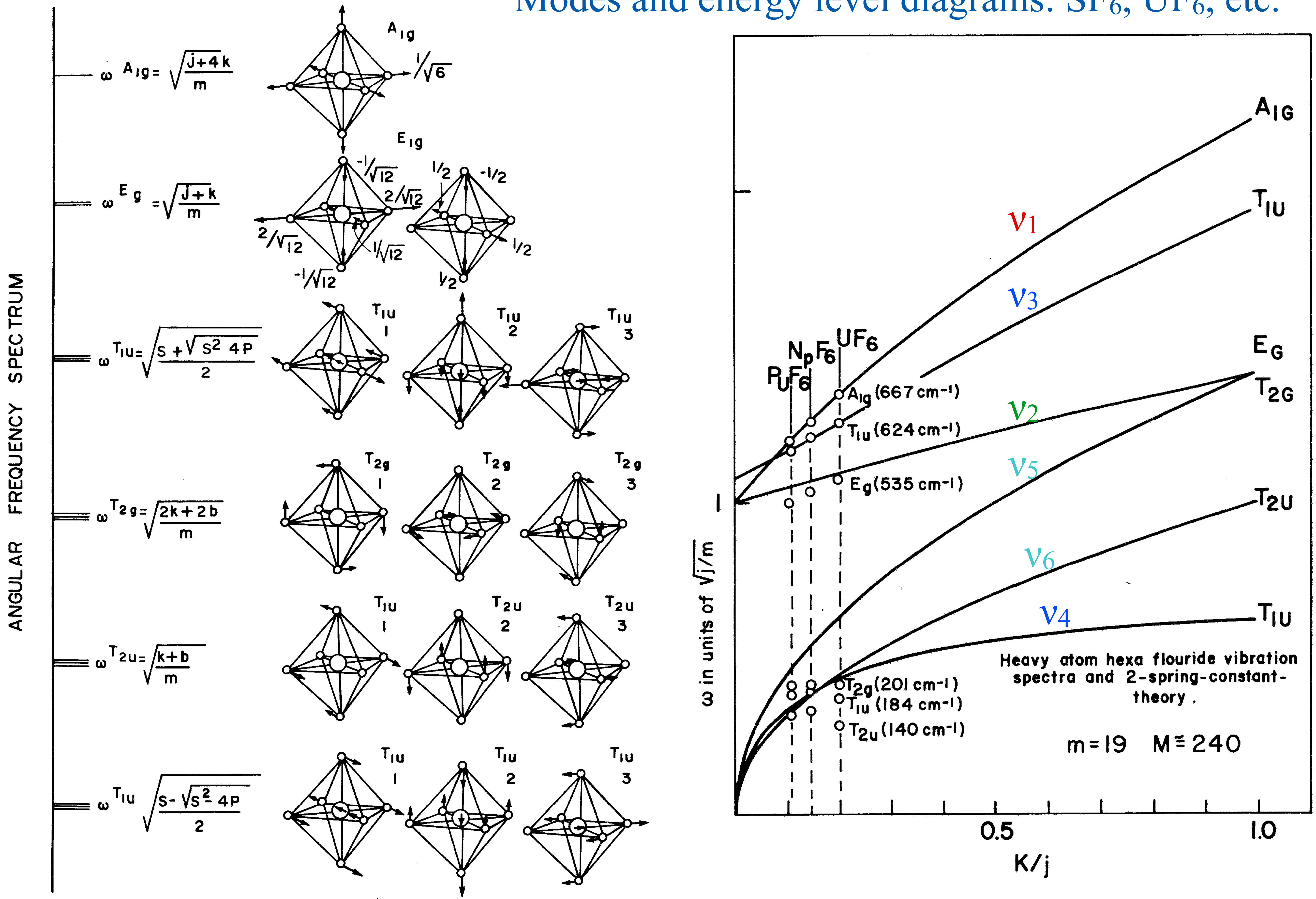

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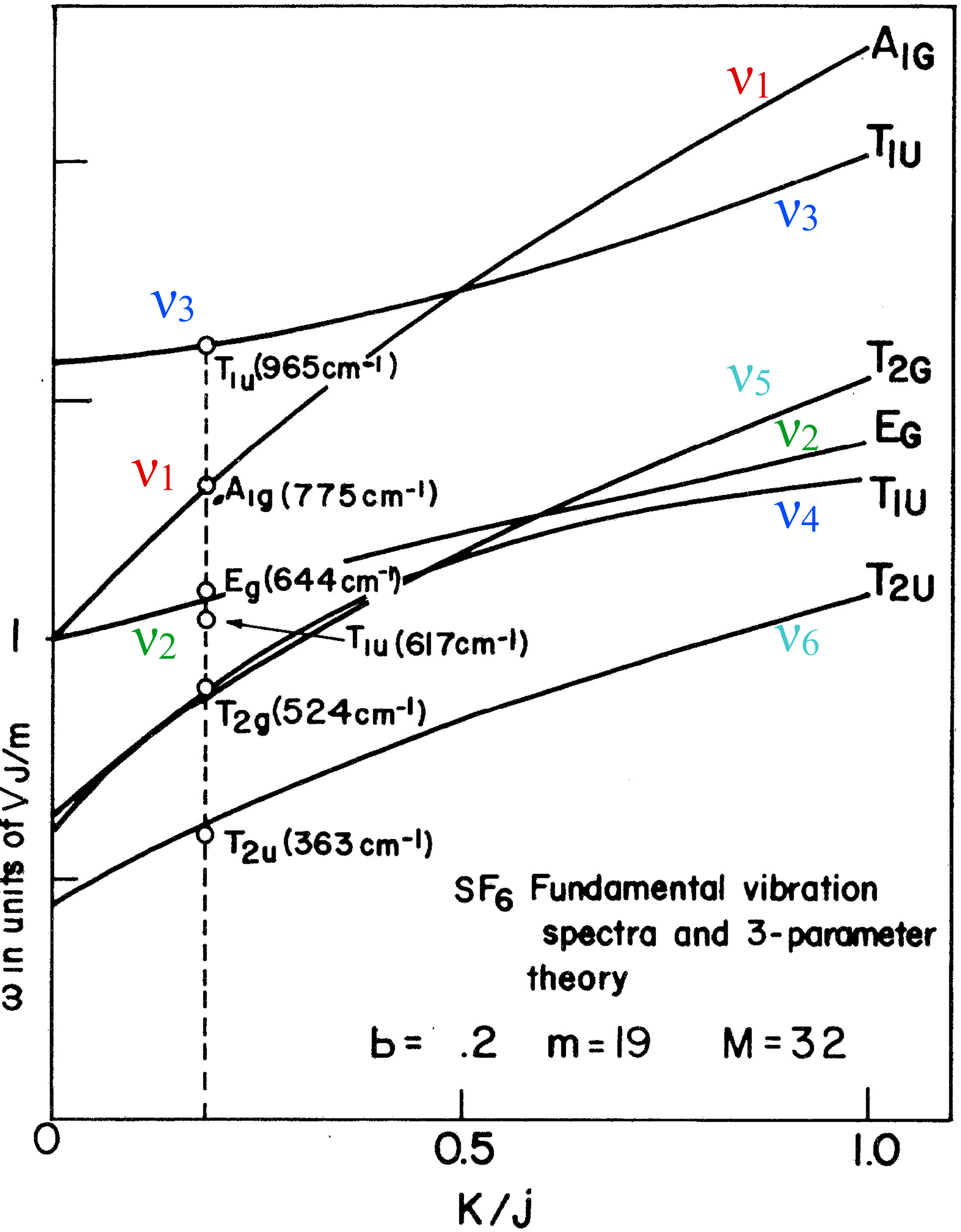

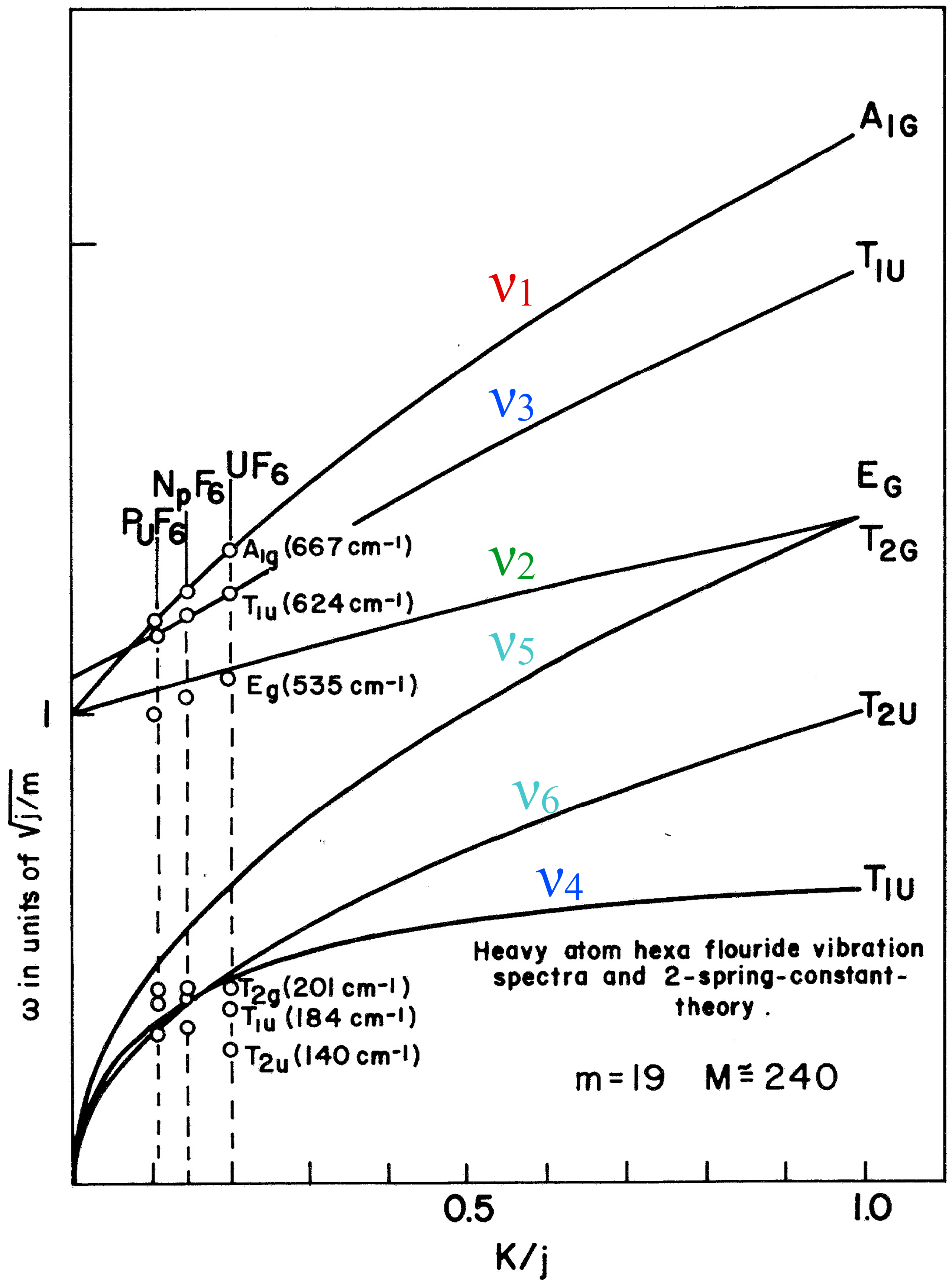

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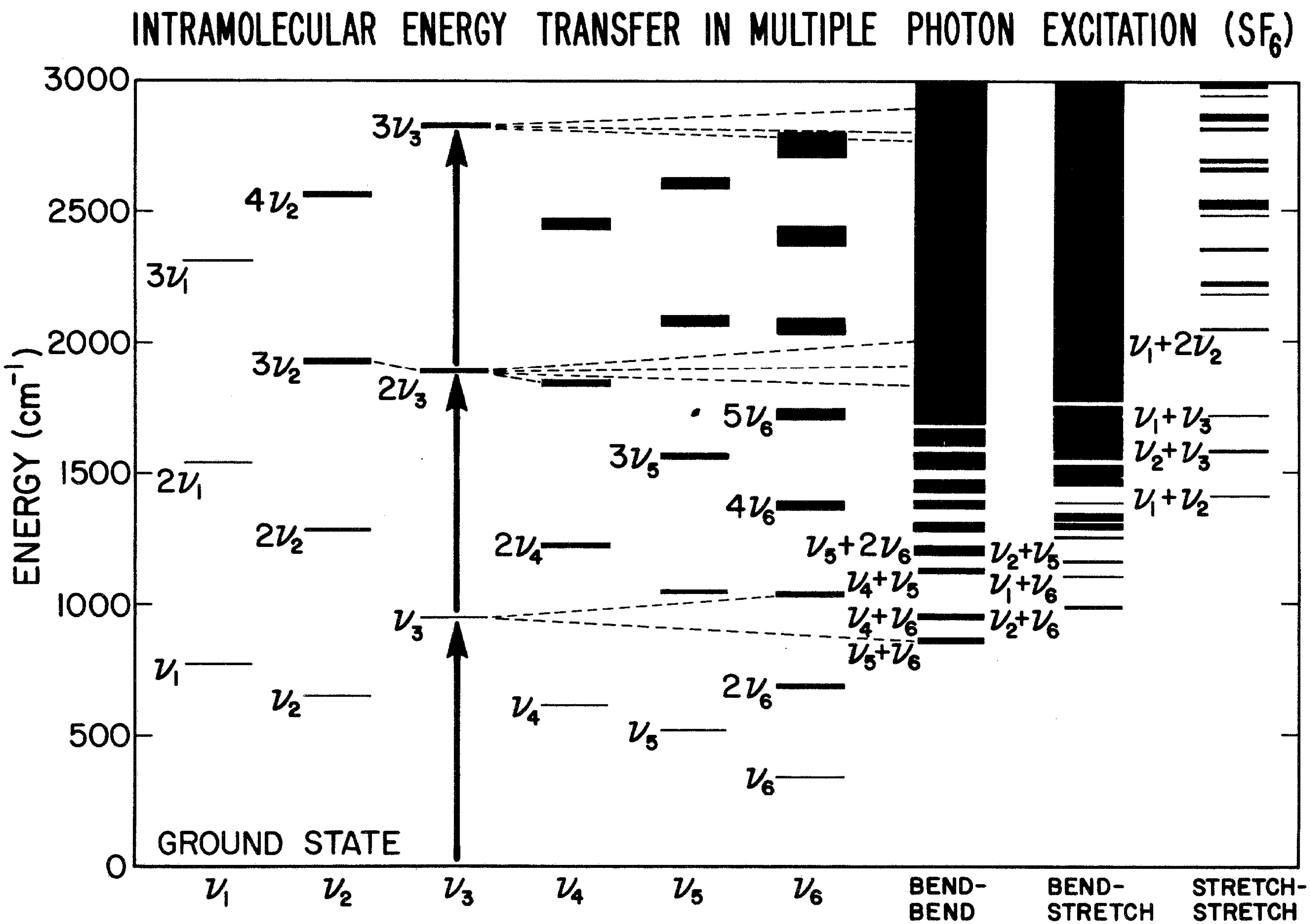

Figure 4.4.8 Sketch of SF_6 quantum vibration levels. The density of levels increases rapidly at higher energy. Standard spectroscopic notation is used. For example, two quanta of the $T_{1u}(+)$ or ν_3 vibration is labeled $2\nu_3$. The figure shows expected flow of energy during laser excitation of the ν_3 "ladder." (Due to Robin S. McDowell and Jay R. Ackerhalt of Los Alamos National Laboratory.)

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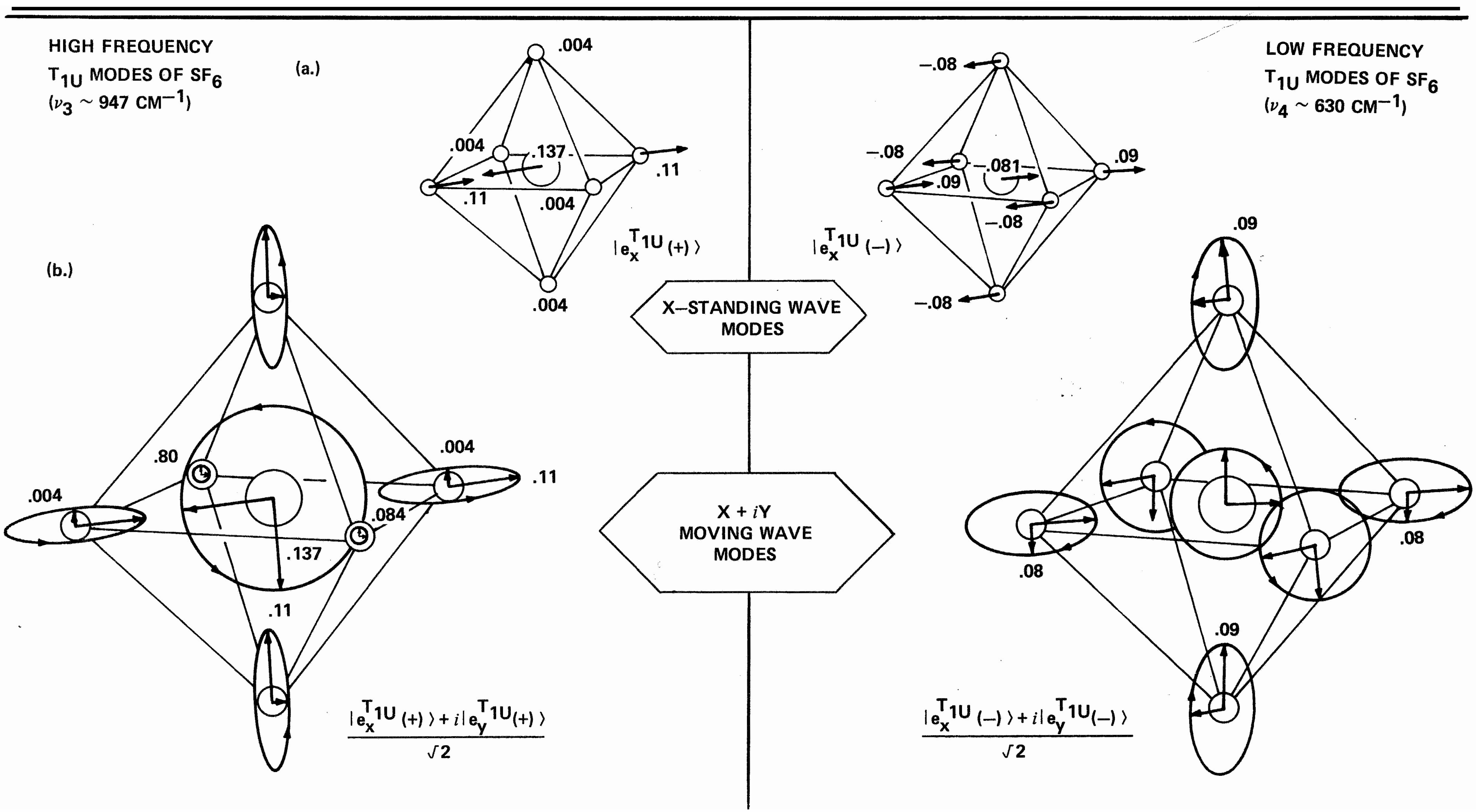

Figure 4.4.7 T_{1u} fundamental motions of $^{32}SF_6$ for high-frequency [ν_3 or (+)] and low-frequency [ν_4 or (−)] vibrations. (a) Plane-polarized or standing-wave motions. (b) Circularly polarized or moving-wave motions.

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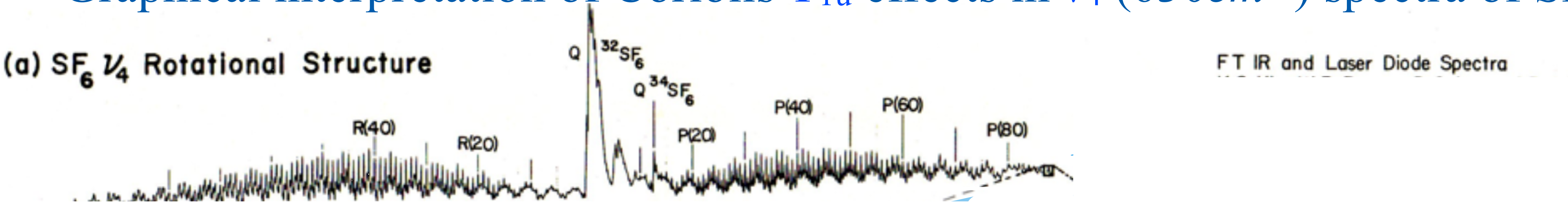
Graphical approach to rotation-vibration-spin Hamiltonian

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

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

Graphical interpretation of Coriolis T_{1u} effects in ν_4 (630cm^{-1}) spectra of SF_6



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

Graphical interpretation of Coriolis T_{1u} effects in ν_4 ($630 cm^{-1}$) spectra of SF_6

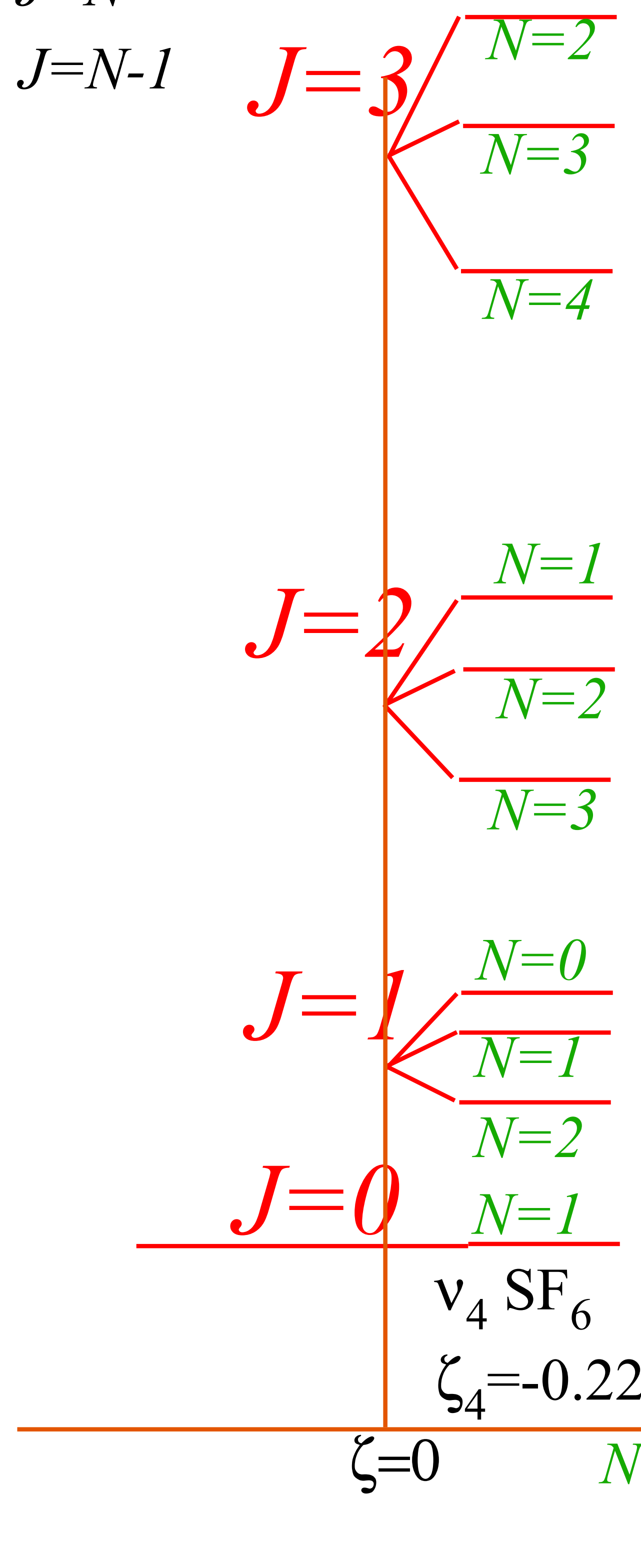
$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

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

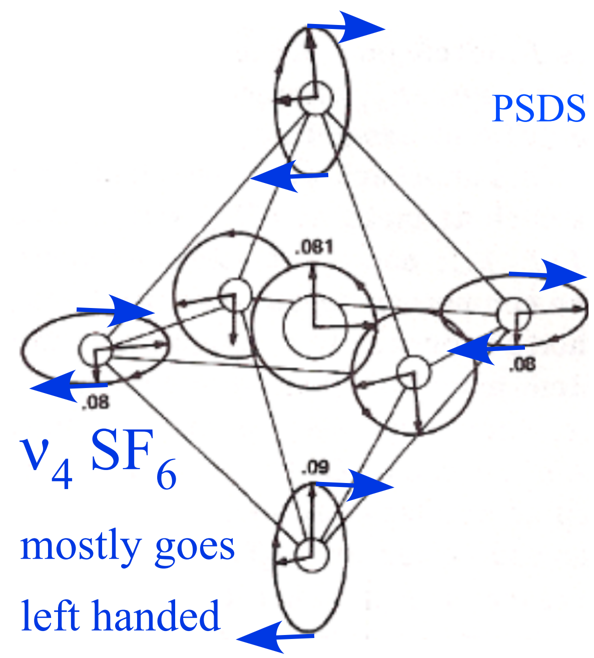
Racah's Trick:

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

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



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



PSDS Ch.4 p.75.

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

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

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

Rotation-polarized
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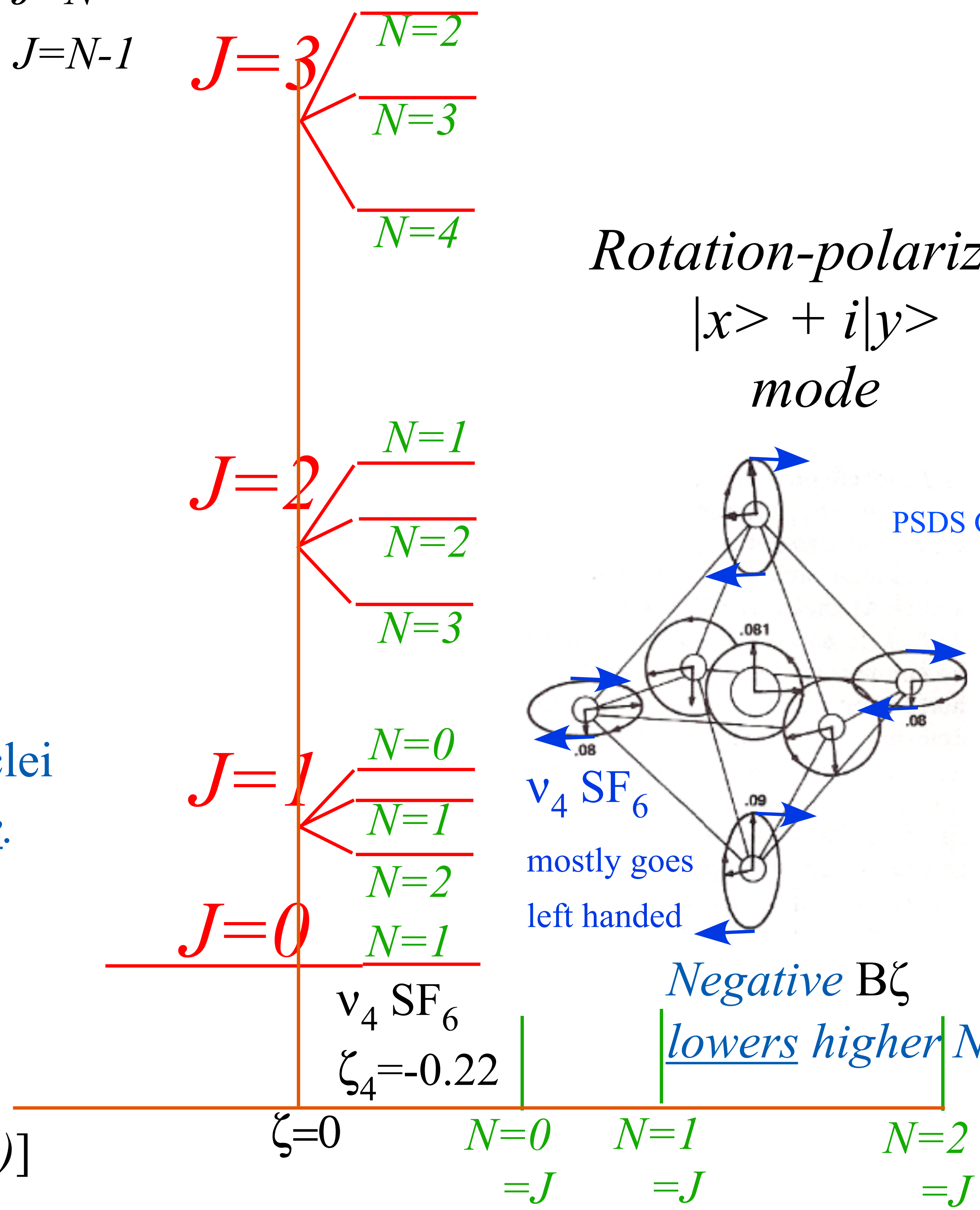

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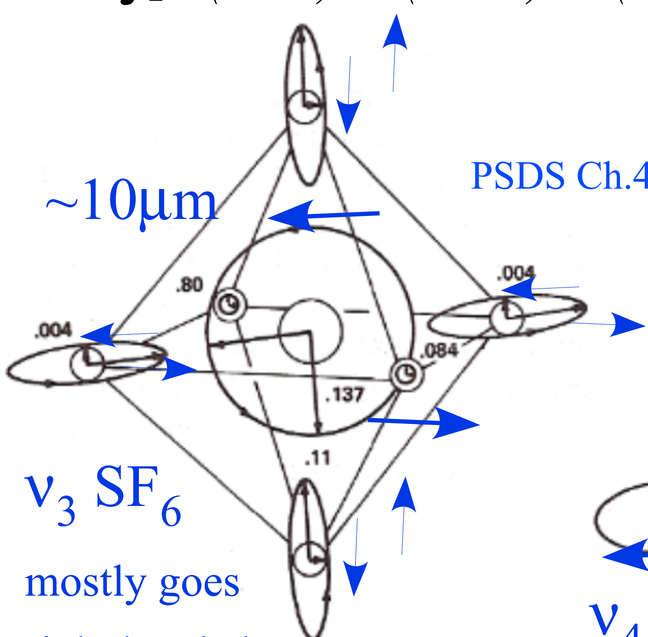
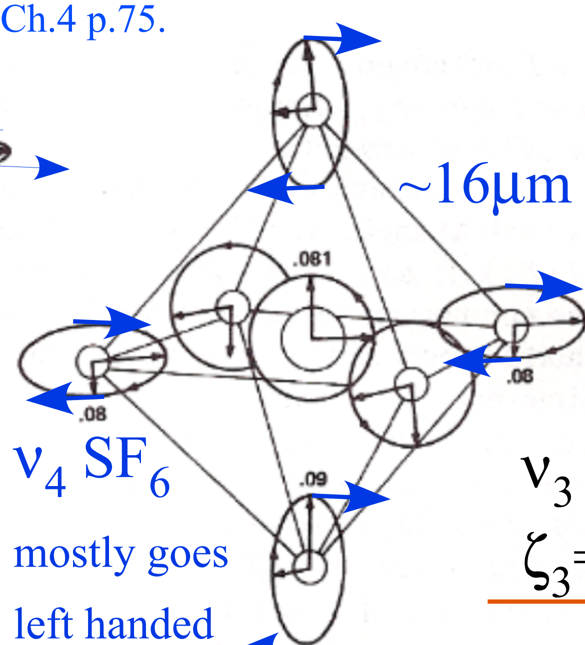


PSDS Ch.4 p.75.

ν_3 SF_6

mostly goes right handed



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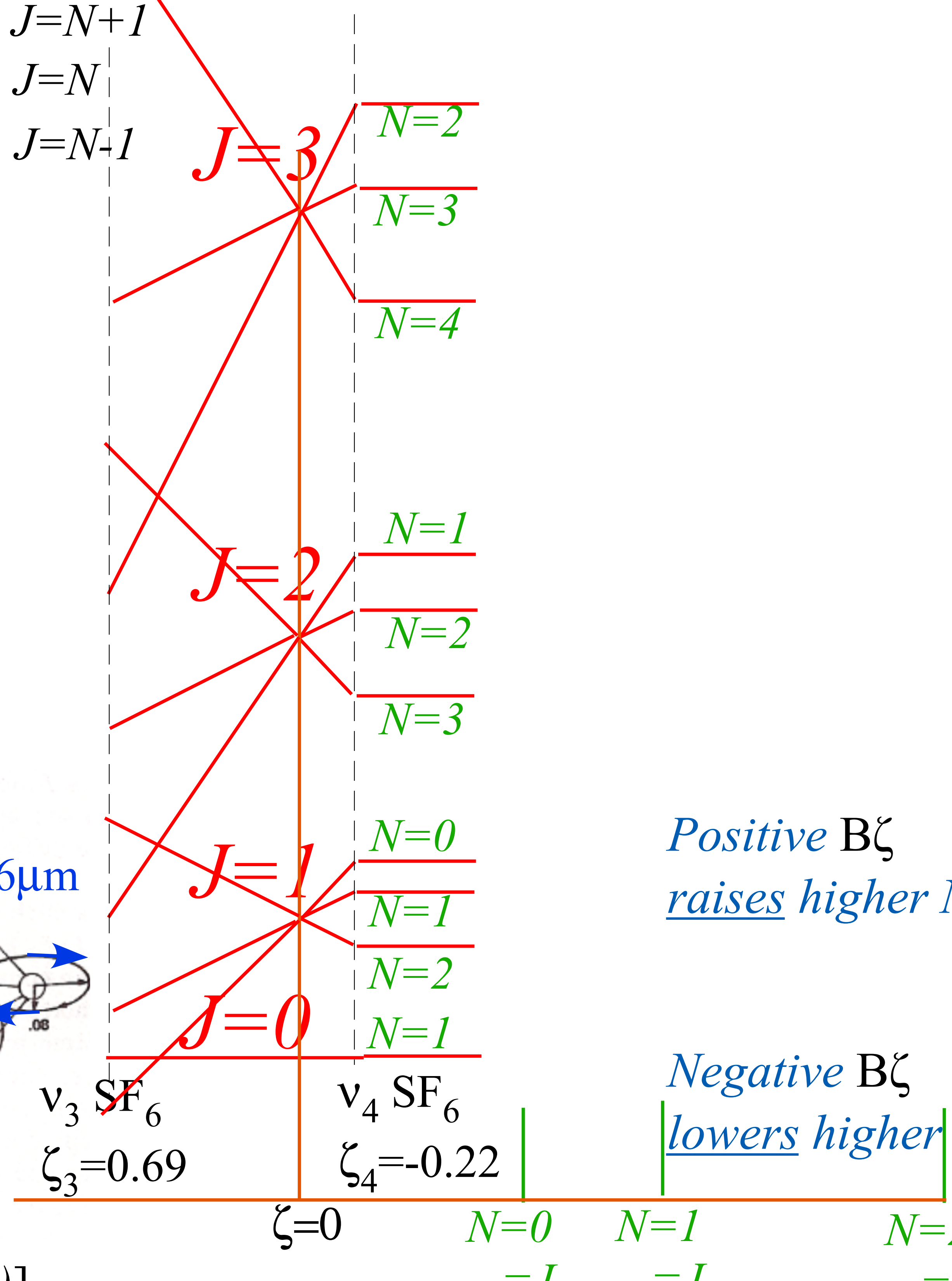

Positive $B\zeta$ *raises higher N*

Negative $B\zeta$ *lowers higher N*

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

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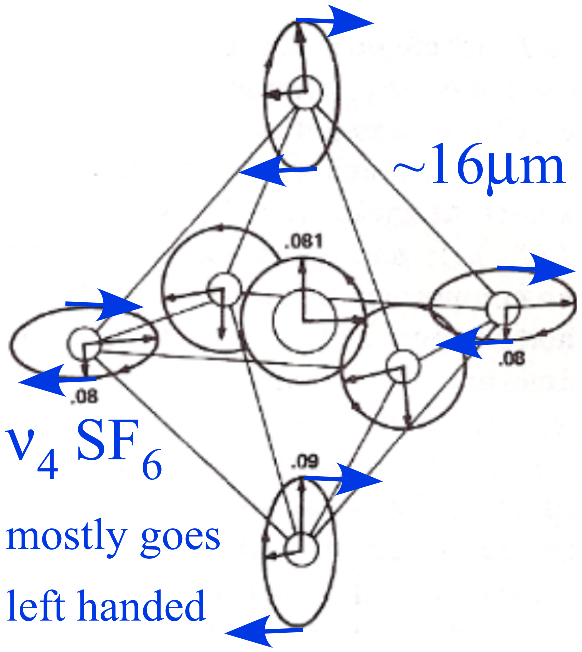

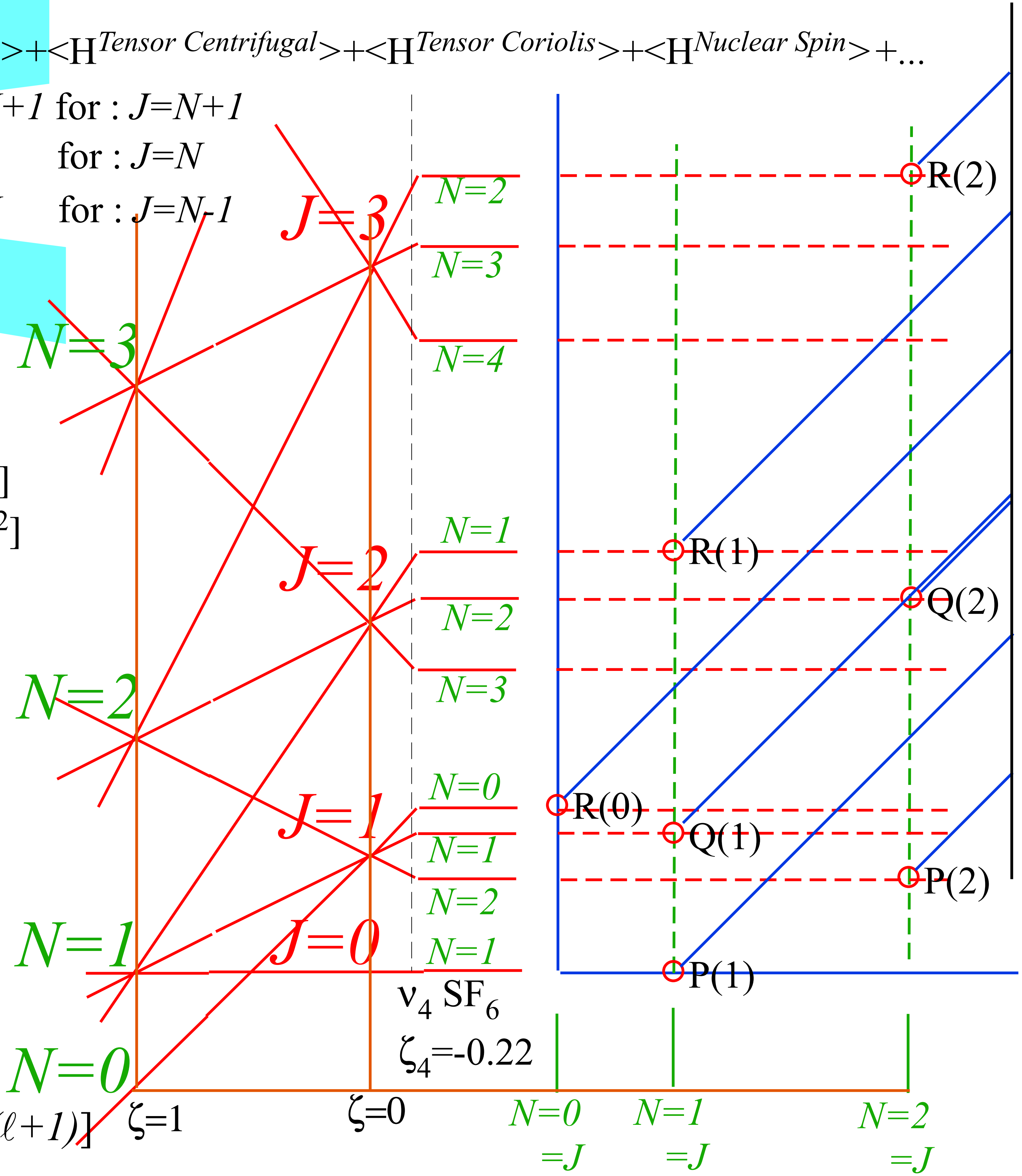

$$= -B\zeta\langle 2\mathbf{J}\cdot\ell\rangle = -B\zeta[J(J+1) - N(N+1) + \ell(\ell+1)]$$

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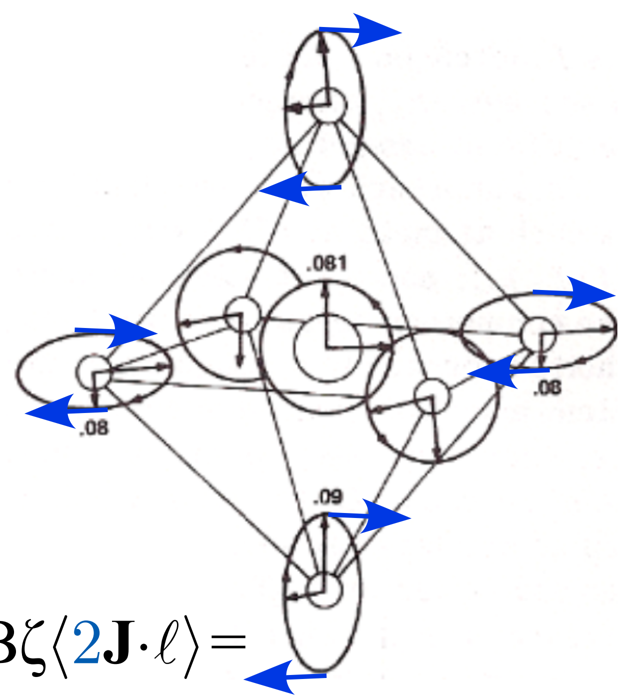
Summary of low-J (PQR) ro-vibe structure

(Using rovib. nomogram)



$-B\zeta\langle 2\mathbf{J}\cdot\ell\rangle =$

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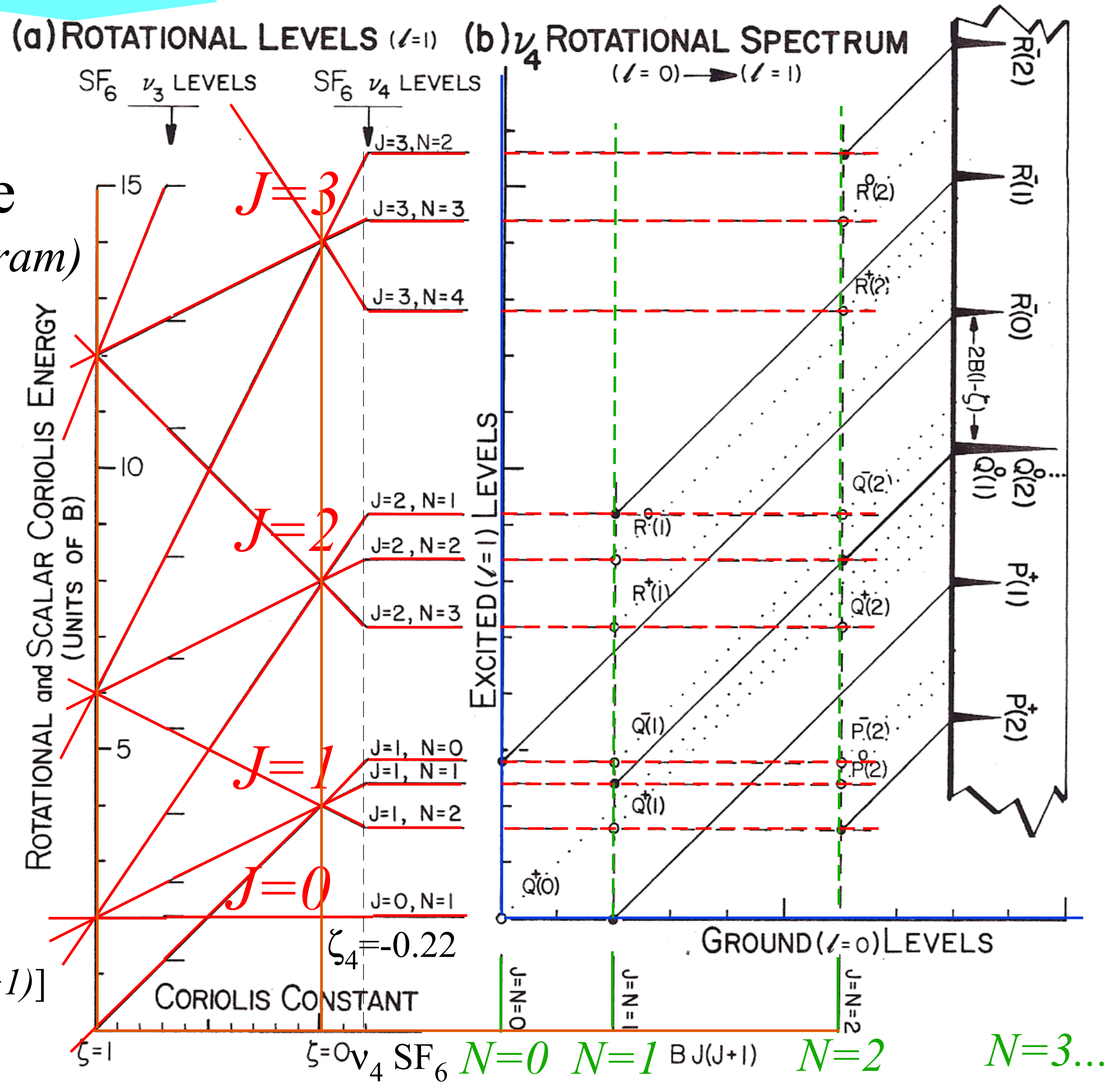

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SF_6 has octahedral ($O_h \supset O \supset C_{4v}$ or C_{3v}) symmetry

SF_6 octahedral ($O_h \supset C_{4v}$) Cartesian coordination

SF_6 octahedral ($O_h \supset C_{4v}$) symmetry coordination

SF_6 octahedral ($O_h \supset C_{4v}$) mode labeling

Ireps for $O \supset D_4 \supset D_2$ subgroup chain and coset factored projectors

Sorting $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ mode vectors

Combining $|T_{1u}\rangle_A$, $|T_{1u}\rangle_B$, and $|T_{1u}\rangle_C$ into two states of zero momentum

Matrices of force **F**, mass **m**, and acceleration **a** for mode dynamics

Acceleration matrix **a** for 2-by-2 T_{1u} ABC-mode dynamics

Modes and energy level diagrams: SF_6, UF_6, etc.

SF_6, overtones and harmonics

Coriolis orbits of T_{1u} modes ν_3 ($947 cm^{-1}$) and ν_4 ($630 cm^{-1}$) of SF_6

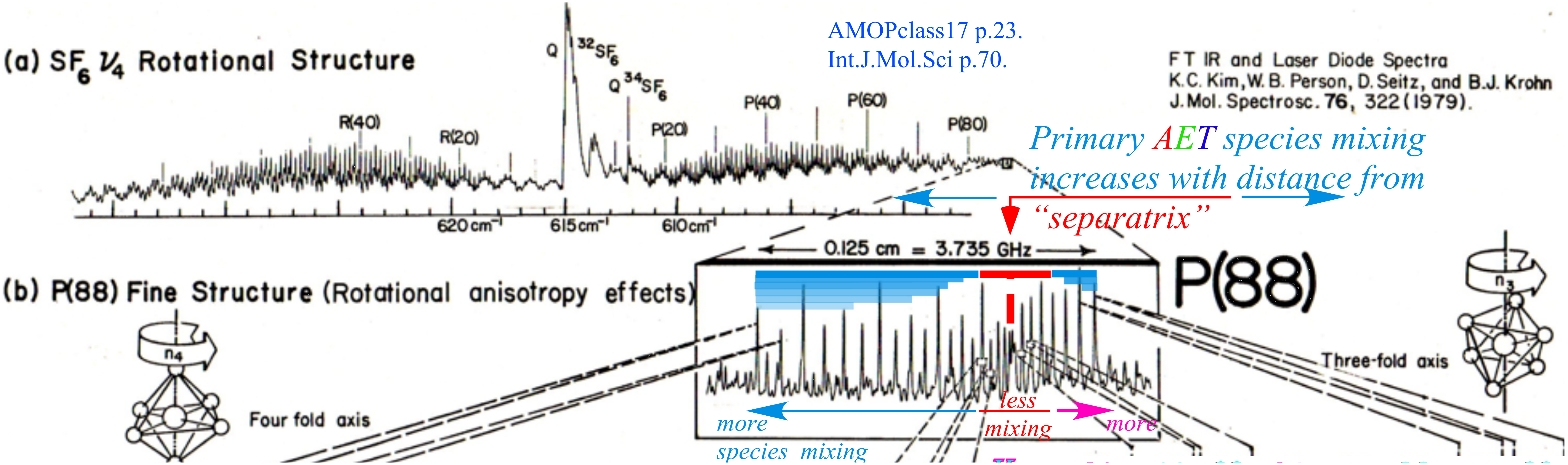
Graphical interpretation of Coriolis T_{1u} effects in ν_4 ($630 cm^{-1}$)

Rovibronic Nomogram of Coriolis T_{1u} effects

Tensor centrifugal and Coriolis T_{1u} effects in ν_4 P(88) fine structure

Nomogram of T_{1u} SF_6 ν_4 P(88) fine, superfine, and hyperfine structure

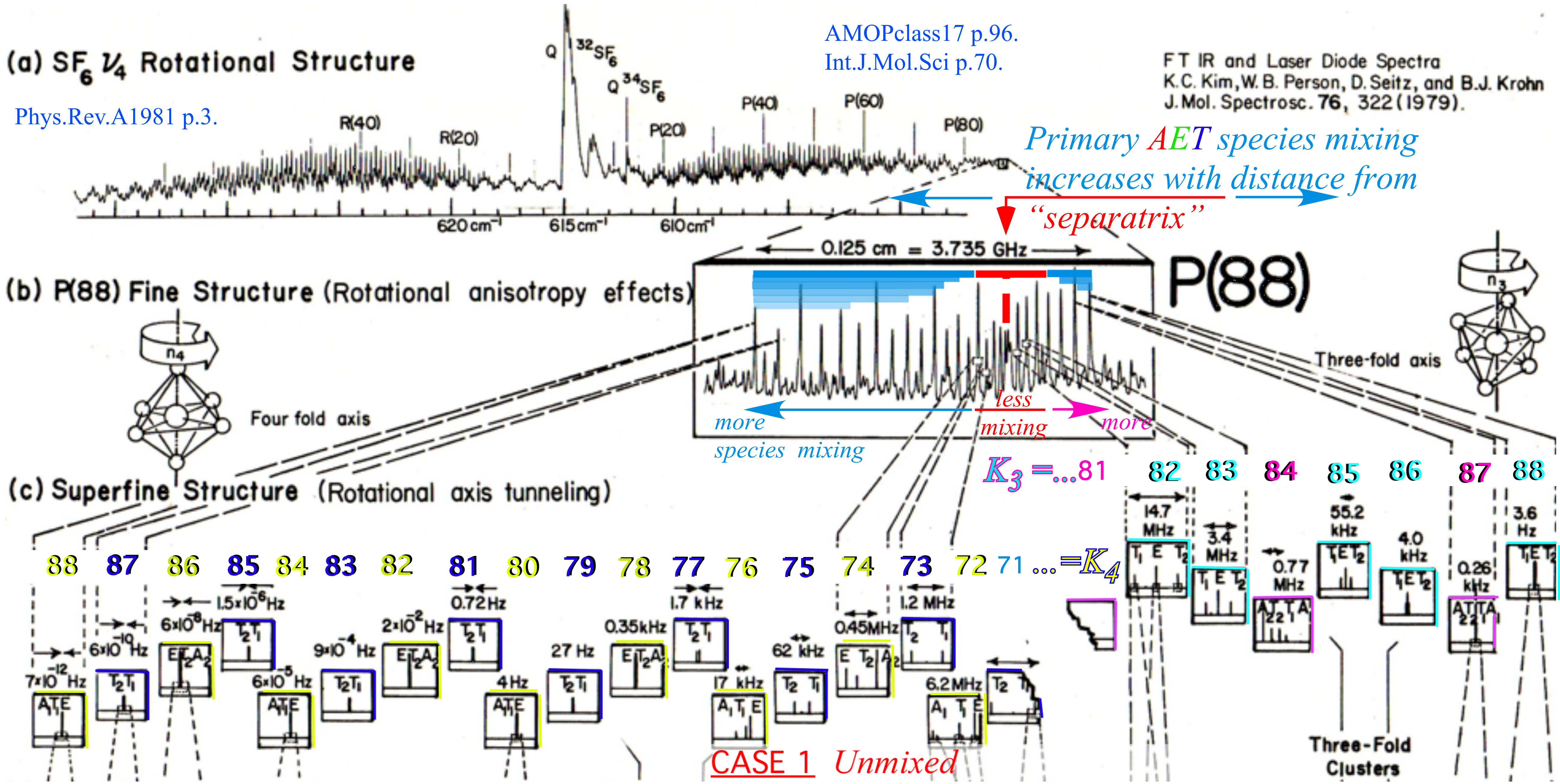
Tensor centrifugal and Coriolis T_{1u} effects in ν_4 P(88) fine structure spectra of SF_6



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

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

Tensor centrifugal and Coriolis T_{1u} effects in ν_4 P(88) superfine spectra of SF_6



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.)*

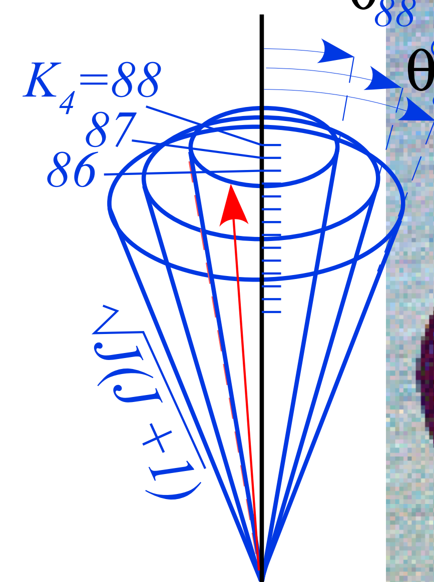
Tensor centrifugal and Coriolis T_{1u} effects in ν_4 ($630 cm^{-1}$) spectra of SF_6

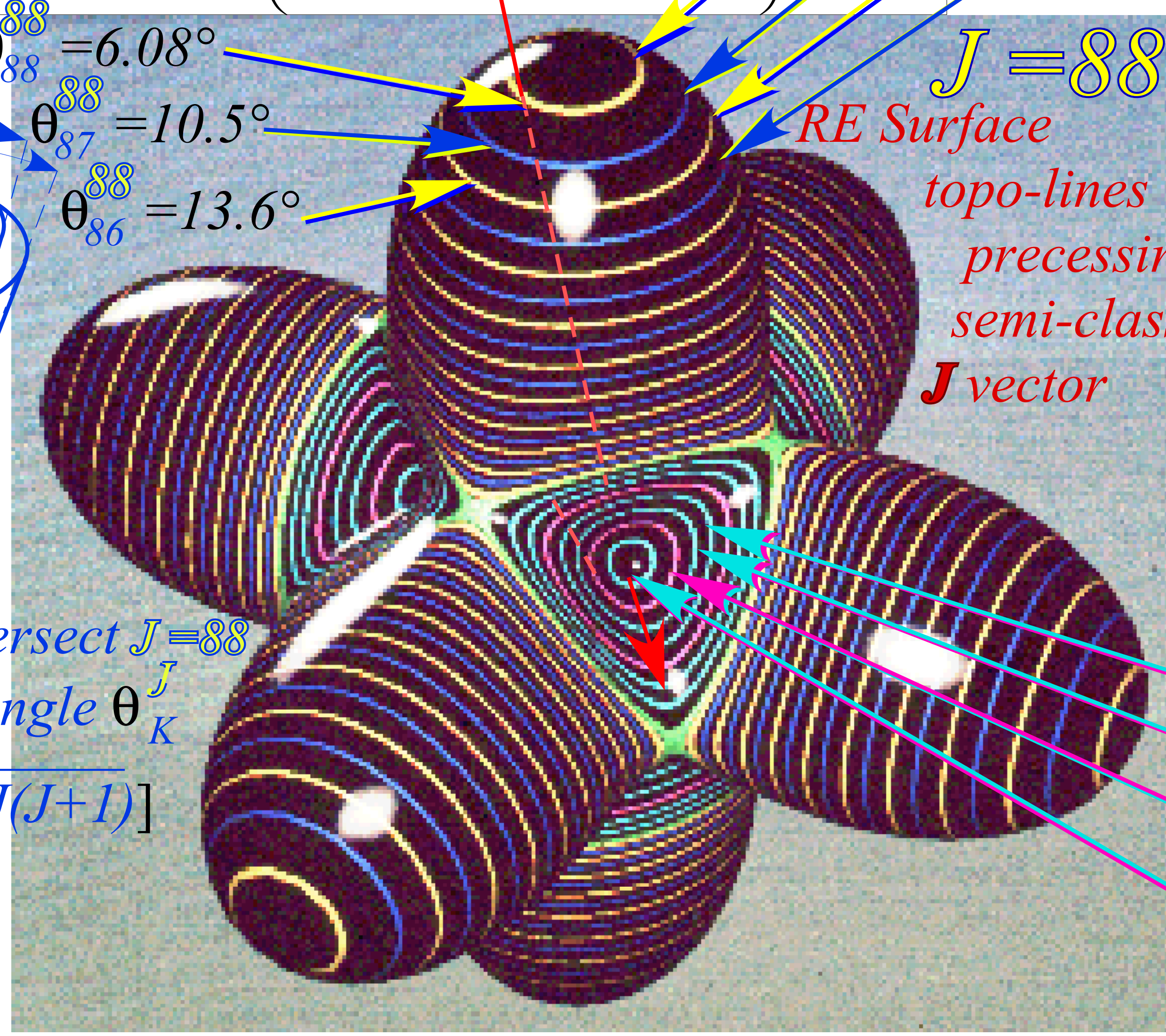
$$\langle H\rangle \sim \nu_{vib} + BJ(J+1) + \langle H^{Scalar\ Coriolis}\rangle + \langle H^{Tensor\ Centrifugal}\rangle + \langle H^{Tensor\ Coriolis}\rangle + \langle H^{Nuclear\ Spin}\rangle + \ldots$$

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

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

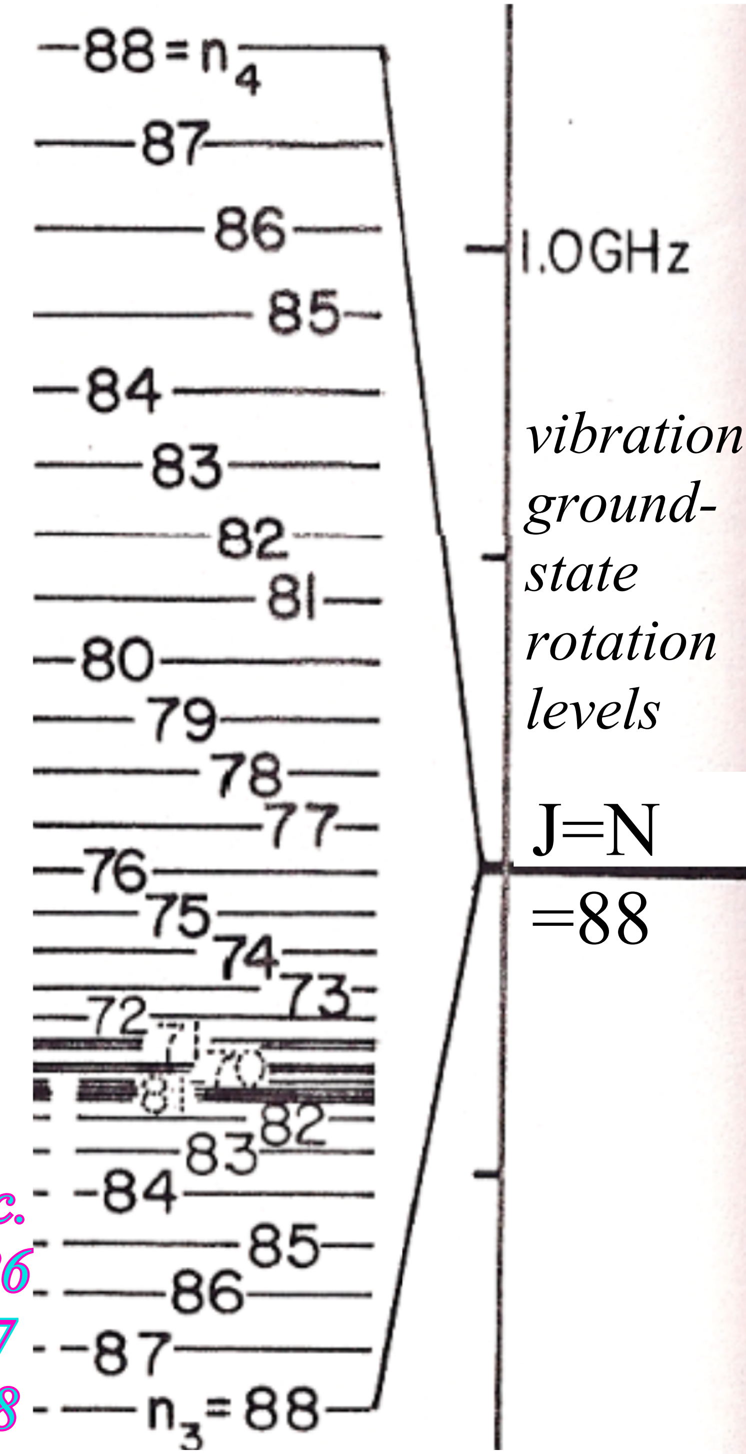
$$= BJ^2 + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$





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

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

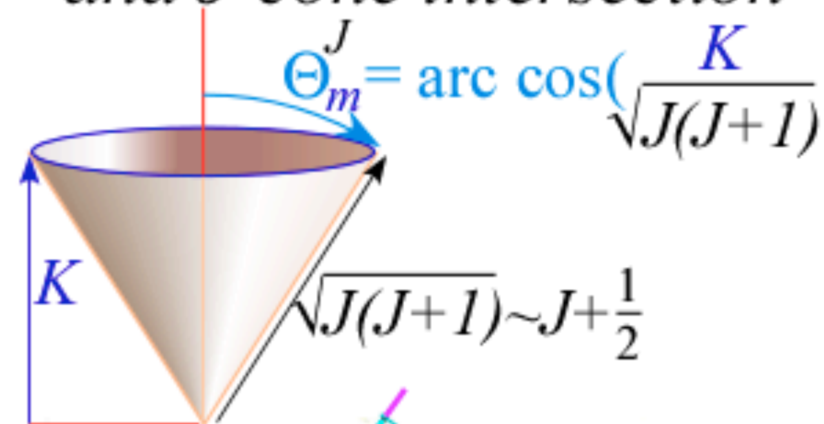


SF_6 Spectra of O_h Ro-vibronic Hamiltonian described by RE Tensor Topography

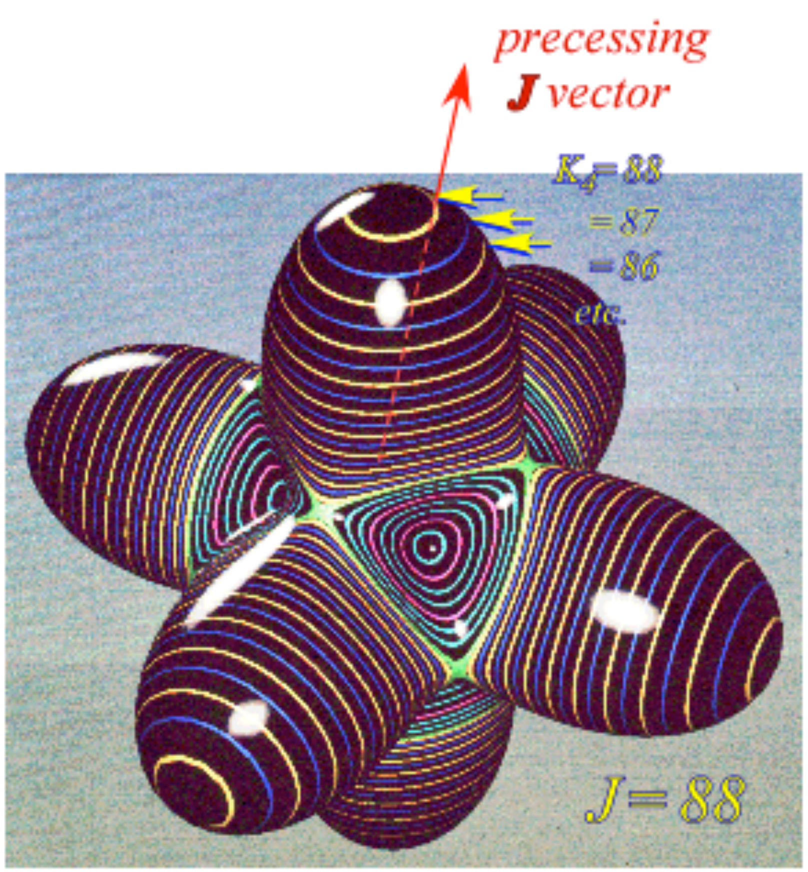
and J-cone intersection

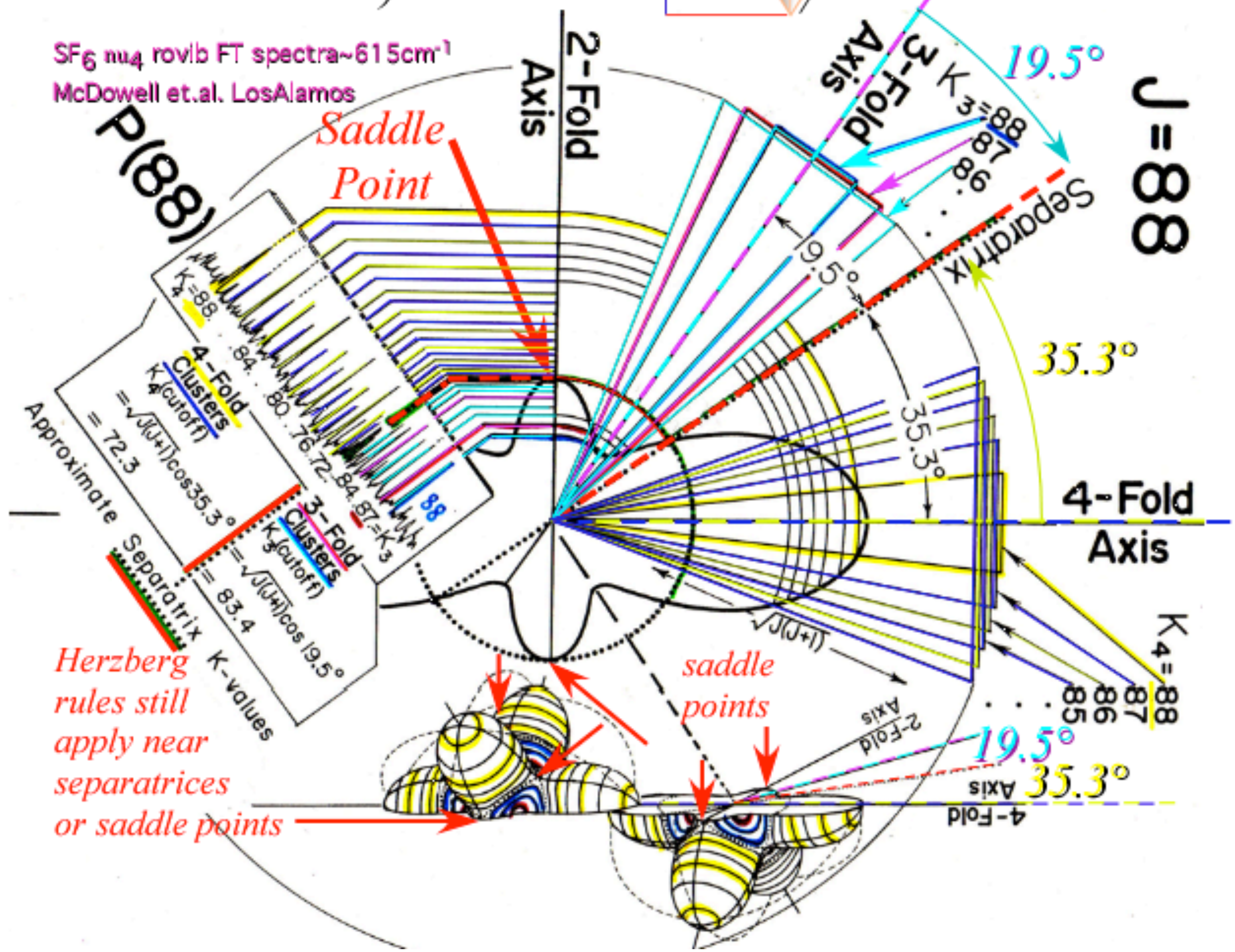
$$\mathbf{H} = B\left(\mathbf{J}_x^2 + \mathbf{J}_y^2 + \mathbf{J}_z^2\right) + t_{440}\left(\mathbf{J}_x^4 + \mathbf{J}_y^4 + \mathbf{J}_z^4 - \frac{3}{5}J^4\right) + \cdots$$

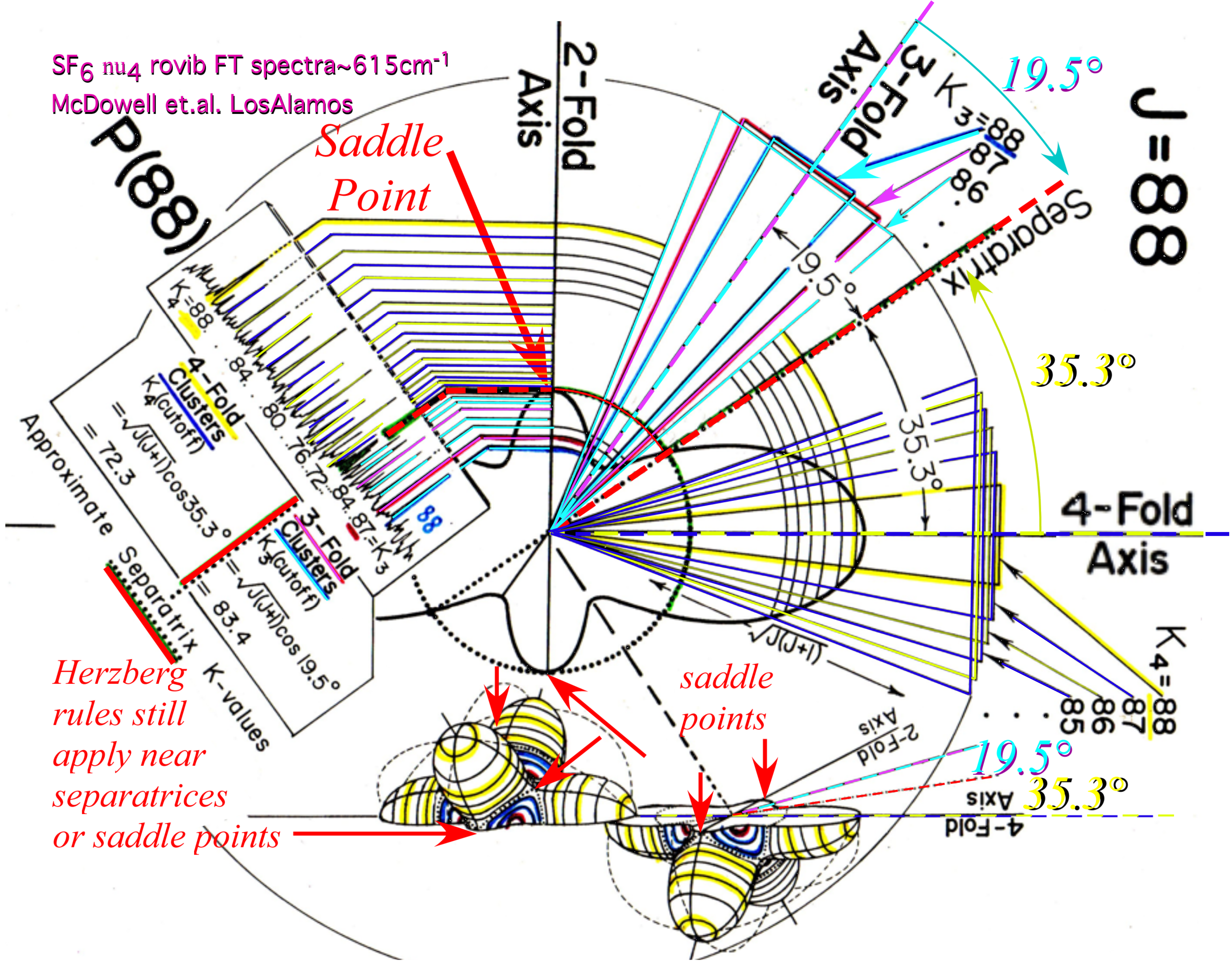
$$= \quad B\mathbf{J}^2 \quad + t_{440}\left(\mathbf{T}_0^4 + \sqrt{\frac{5}{14}}\left[\mathbf{T}_4^4 + \mathbf{T}_{-4}^4\right]\right) + \cdots$$



Rovibronic Energy (RE) Tensor Surface







SF6 nu4 rovib FT spectra~615cm-1
McDowell et.al. LosAlamos
P(88)
Saddle Point
2-Fold Axis
3-Fold Axis
19.5°
J=88
K3=88
87
86
Separatrix
9.5°
35.3°
4-Fold Axis
K4=88
84
80
76
72
84
87=K3
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)
K4=88
87
86
85
saddle points
2-Fold Axis
4-Fold Axis
Herzberg rules still apply near separatrices or saddle points

AMOP reference links on pages 2-4

4.30.18 class 27: *Symmetry Principles for Advanced Atomic-Molecular-Optical-Physics*

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➡ Nomogram of T_{1u} SF_6 ν_4 P(88) fine, superfine, and hyperfine structure

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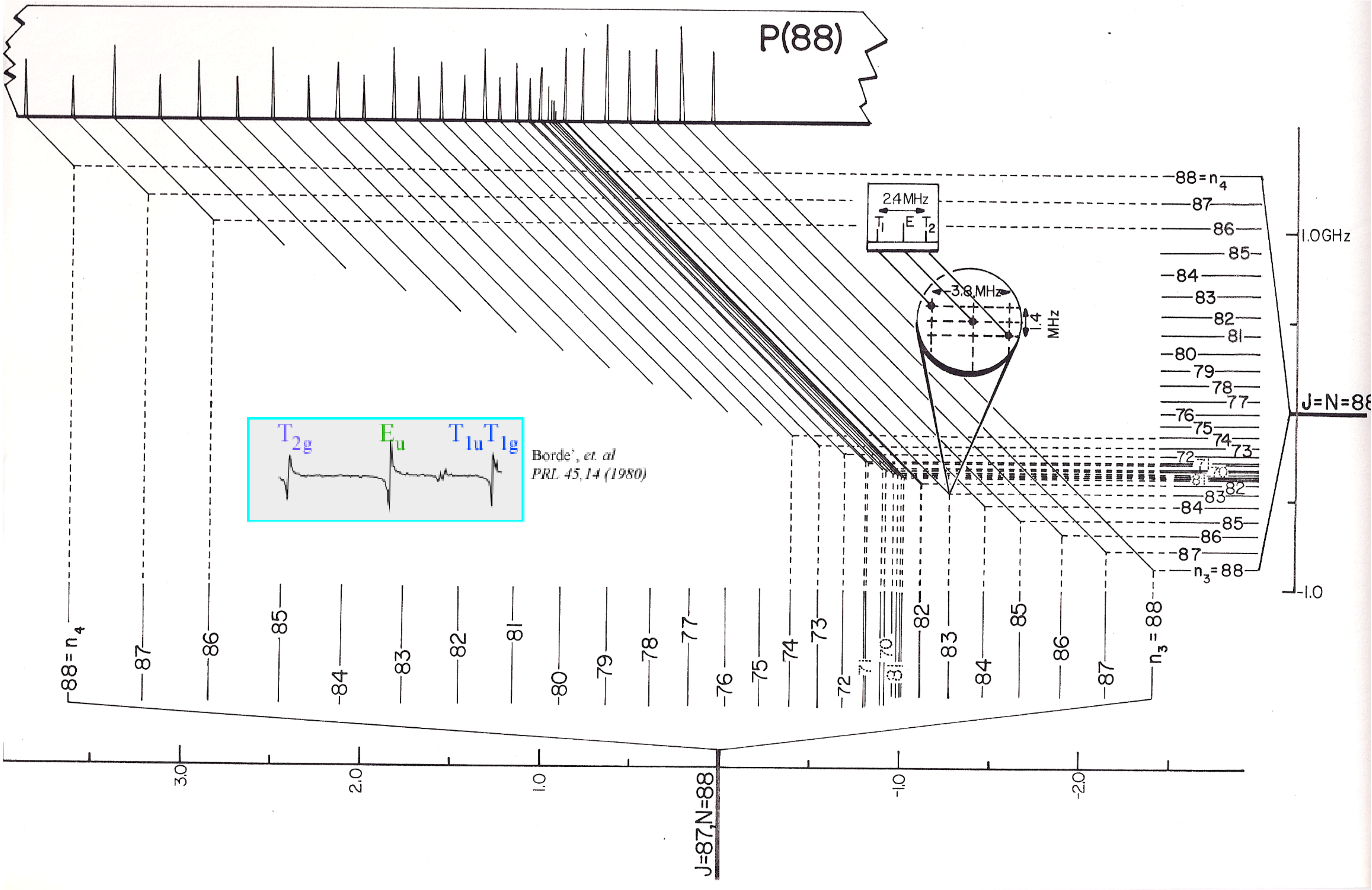


Borde', et. al PRL 45,14 (1980)

Graphical approach to rotation-vibration-spin Hamiltonian

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

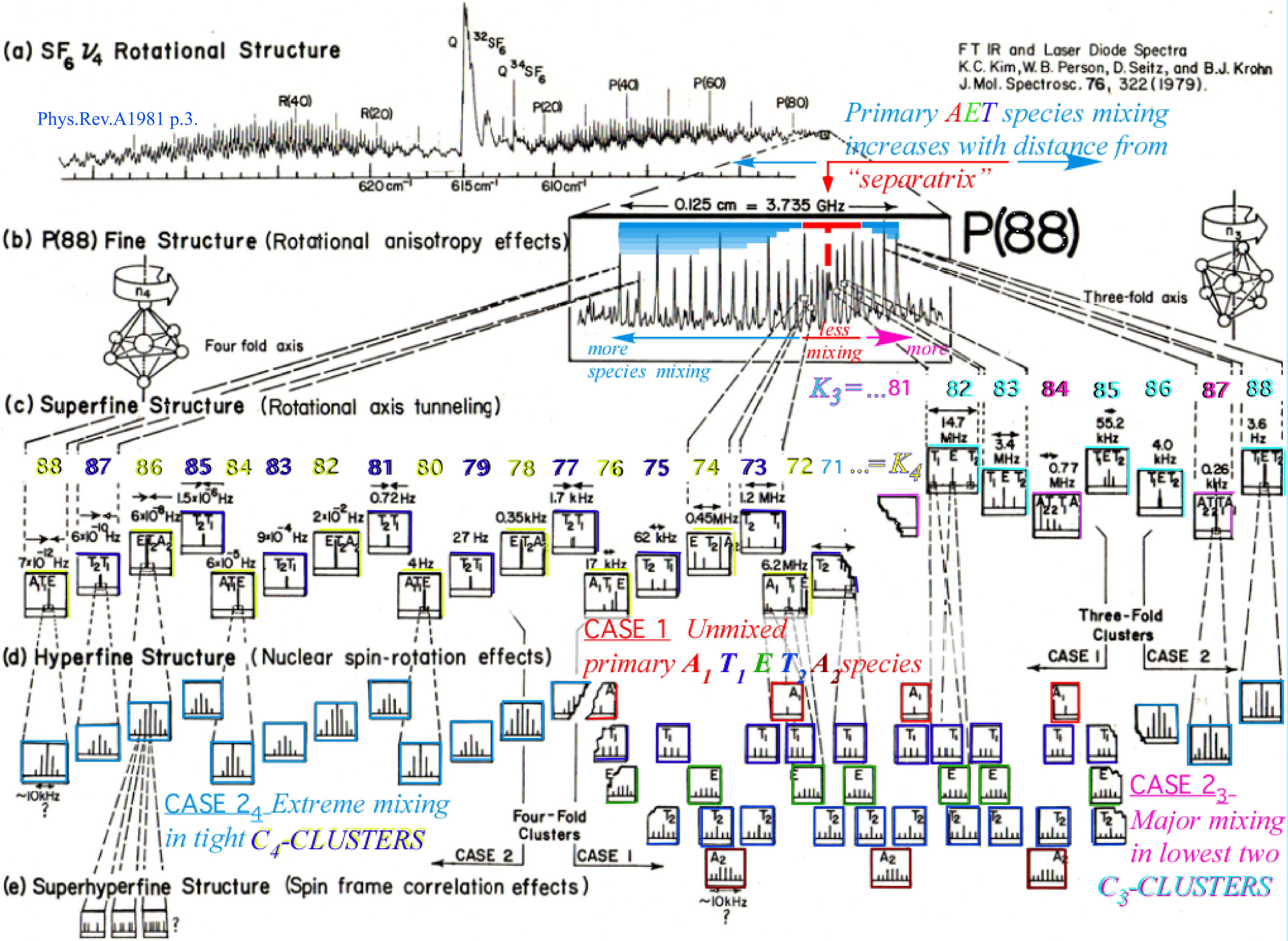
OUTLINE

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) SF_6 ν_4 Rotational Structure
Phys.Rev.A1981 p.3.
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
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
(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)
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
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
Three-Fold Clusters
CASE 1
CASE 2
CASE 1 Unmixed
primary A_1 T_1 E T_2 A_2 species
(d) Hyperfine Structure (Nuclear spin-rotation effects)
~10 kHz
?
CASE 2_4 Extreme mixing
in tight C_4-CLUSTERS
Four-Fold Clusters
CASE 2
CASE 1
CASE 2_3-
Major mixing
in lowest two
C_3-CLUSTERS
~10 kHz
?
(e) Superhyperfine Structure (Spin frame correlation effects)
?

$\langle F \rangle =$

	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
$\langle A\|$	$2k+j$	0	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	$\frac{k}{2}$	0	0	0	$\frac{-k}{2}$	$\frac{-k}{2}$	0	0	$\frac{k}{2}$	0	0	$\frac{-k}{2}$	0	0	0	$-j$
$\langle B\|$							$k+b$	0	0	0	0	0	0	$\frac{-(k+b)}{2}$	0	0	$\frac{-(k+b)}{2}$	0	$\frac{-b}{2}$	0	0
$\langle C\|$																			$2(j+b)$	0	0

$\langle m \rangle =$

	$\|1\rangle_A$	$\|R_1^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|1\rangle_B$	$\|r_1\rangle$	$\|r_2\rangle$	$\|r_1^2\rangle$	$\|r_4^2\rangle$	$\|R_2^2\rangle$	$\|R_1\rangle$	$\|R_2\rangle$	$\|R_3\rangle$	$\|R_1^3\rangle$	$\|R_2^3\rangle$	$\|i_3\rangle$	$\|1\rangle_C$	$\|2\rangle$	$\|3\rangle$
$\langle A\|$	m	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\langle B\|$							m	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$\langle C\|$																			M	0	0