LECTURE #3:

THE ROLE OF SYMMETRY IN HIGH-RESOLUTION SPECTROSCOPY

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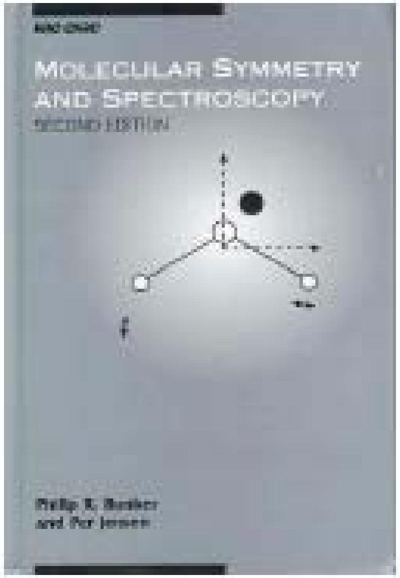
OUTLINE

- Introduction
- CNP and CNPI groups
- Molecular symmetry (MS) groups
- Spin statistical weights
- Summary

Some of the relevant literature on molecular symmetry of rovibronic states

- P. R. Bunker and P. Jensen: *Molecular Symmetry and Spectroscopy*, 2nd edition, NRC Research Press, Ottawa, 1998
- H. C. Longuet-Higgins: *Mol. Phys*. **6**, 445 (1963)
- J. T. Hougen, *J. Chem. Phys*. **39**, 358 (1963)
- M. Quack: Fundamental symmetries and symmetry violation from high-resolution spectroscopy, *Handbook of High-Resolution Spectroscopy*, Wiley: 2011



Fundamental symmetries of molecular physics

(1) translation in space ($\boldsymbol{G}_{\mathrm{T}}$) – uniform space

(2) translation in time

(3) rotation in space ($\boldsymbol{K}$(spatial)) – isotropic space

(4) inversion of all particle coordinates at the origin (space inversion, parity operation P)

(5) „time reversal" or the reversal of all particle momenta including spin but not the coordinates (operation T for time reversal, antiunitary)

(6) permutation of indices of identical particles ($\boldsymbol{S}_{\mathrm{n}}^{(\mathrm{e})}$ and $\boldsymbol{G}^{\mathrm{CNP}}$)

(7) replacement of all particles by their corresponding antiparticles (operation C for charge conjugation, *e*.*g*., electrons vs. positrons)

Fundamental symmetries of molecular physics

exact symmetry ––> exact conservation law

- (1) ––> momentum conservation
- (2) ––> energy conservation
- (3) ––> angular momentum conservation
- (4) ––> parity conservation

P, *C*, and *T*, as well as *CP* are all individually violated, only *CPT* remains an exact symmetry in the current „standard model”

source: M. Quack

Symmetry and molecules with internal motion (rotation and vibration)

- concept: the symmetry operations considered leave the molecular Hamiltonian unchanged (invariant) and not the geometrical symmetry of the equilibrium structure (like point group symmetries)
- such **symmetry groups** have elements of permutations of identical nuclei with or without inversion
- symmetry operations considered: **feasible permutation-inversion** operations
- symmetry groups have properties similar to those of the well known point groups: irreducible representations, classes, characters, etc.

Permutation (symmetric) groups

- *permutation*: change the order of an ordered string of numbers, a list (*e.g.*, 1, 2, and 3 can be arranged in 3! = 6 ways: $\underline{123}$, $\underline{132}$, $\underline{213}$, $\underline{231}$, $\underline{312}$, $\underline{321}$)
- *permutational operator*: operates on a list and performs a replacement [$(13)\underline{213} = \underline{231}$]
- *transposition*: (12), (13), etc. [$(12) \equiv (21)$]
- *cycles*: (123), (132), etc.
- (123) (132) = *E* (*identity operation*)

$$(ab...z) = \begin{pmatrix} a & b & c & \cdots & y & z \\ b & c & d & \cdots & z & a \end{pmatrix}$$

Permutation (symmetric) groups

Successive application of permutations:

$$(23)(132) = \begin{pmatrix} 123 \\ 132 \end{pmatrix}\begin{pmatrix} 123 \\ 312 \end{pmatrix} = \begin{pmatrix} 312 \\ 213 \end{pmatrix}\begin{pmatrix} 123 \\ 312 \end{pmatrix} = \begin{pmatrix} 123 \\ 312 \\ 213 \end{pmatrix} = \begin{pmatrix} 123 \\ 213 \end{pmatrix} = (12)$$

breaking down a permutation into products of transpositions is not unique but the number of transpositions (odd/even) is (relation to Bose-Einstein and Fermi-Dirac statistics)

transpositions are the *inverses* of themselves

defined everything to form a group: *permutation group* (*symmetric group*)

S_3 group

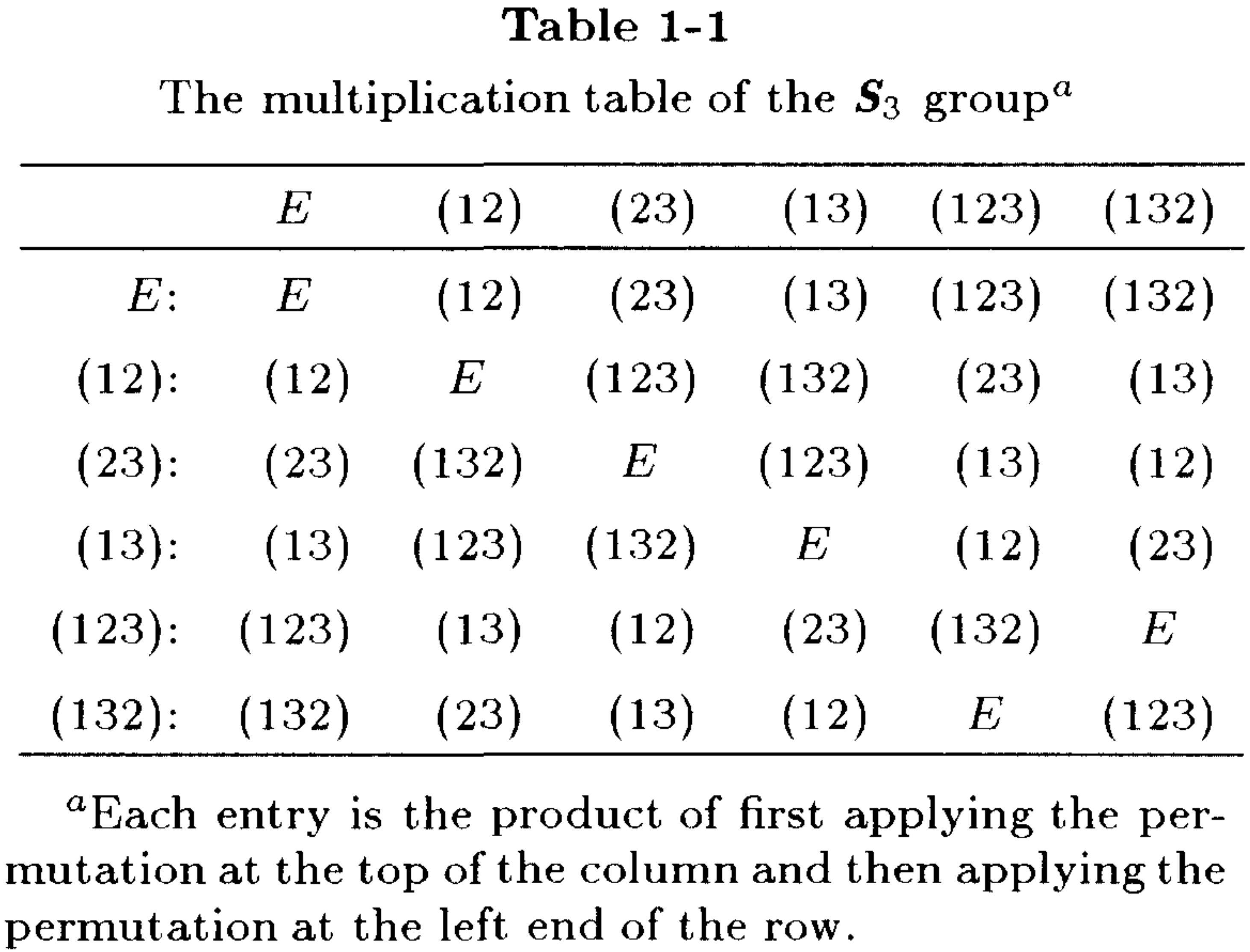


Table 1-1

The multiplication table of the S_3 group[a]

	E	(12)	(23)	(13)	(123)	(132)
E:	E	(12)	(23)	(13)	(123)	(132)
(12):	(12)	E	(123)	(132)	(23)	(13)
(23):	(23)	(132)	E	(123)	(13)	(12)
(13):	(13)	(123)	(132)	E	(12)	(23)
(123):	(123)	(13)	(12)	(23)	(132)	E
(132):	(132)	(23)	(13)	(12)	E	(123)

[a] Each entry is the product of first applying the permutation at the top of the column and then applying the permutation at the left end of the row.

source: P.R. Bunker, P. Jensen

CNP group

Application to molecules: the *complete nuclear permutation* (CNP) group of a molecule containing *l* identical nuclei of one set, *m* of another, etc., is the following direct product:

$$\boldsymbol{G}^{\mathrm{CNP}} = \boldsymbol{S}_l \otimes \boldsymbol{S}_m \otimes \boldsymbol{S}_n \otimes \cdots$$

Example: CNP group of CHO-COOH.

$$\begin{aligned}\boldsymbol{G}^{\mathrm{CNP}} &= \boldsymbol{S}_3^{(\mathrm{O})} \otimes \boldsymbol{S}_2^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})} \\ &= \{E, (12), (23), (13), (123), (132)\} \otimes \{E, (45)\} \otimes \{E, (67)\}\end{aligned}$$

The complete list contains 3! x 2! x 2! = 24 elements.

source: P.R. Bunker, P. Jensen

12 distinct forms of ethylene

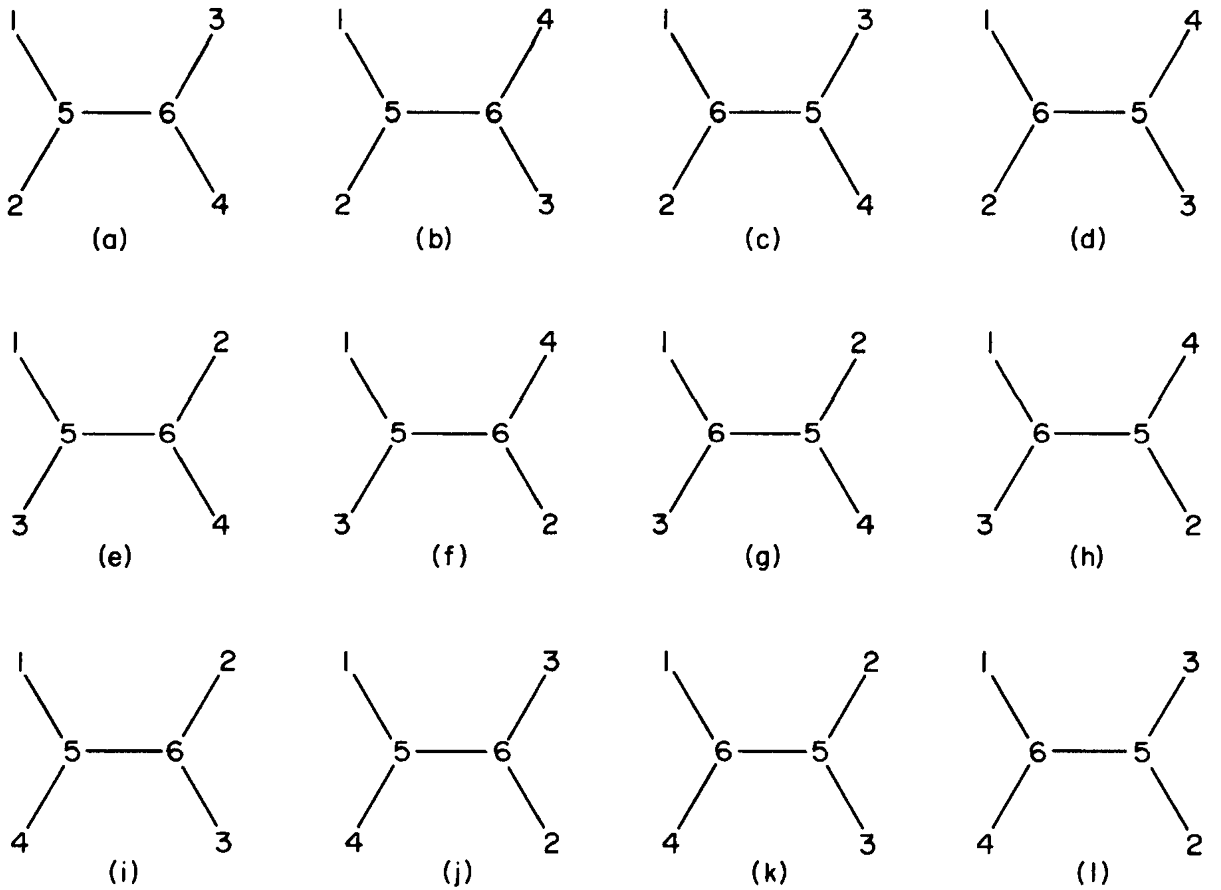


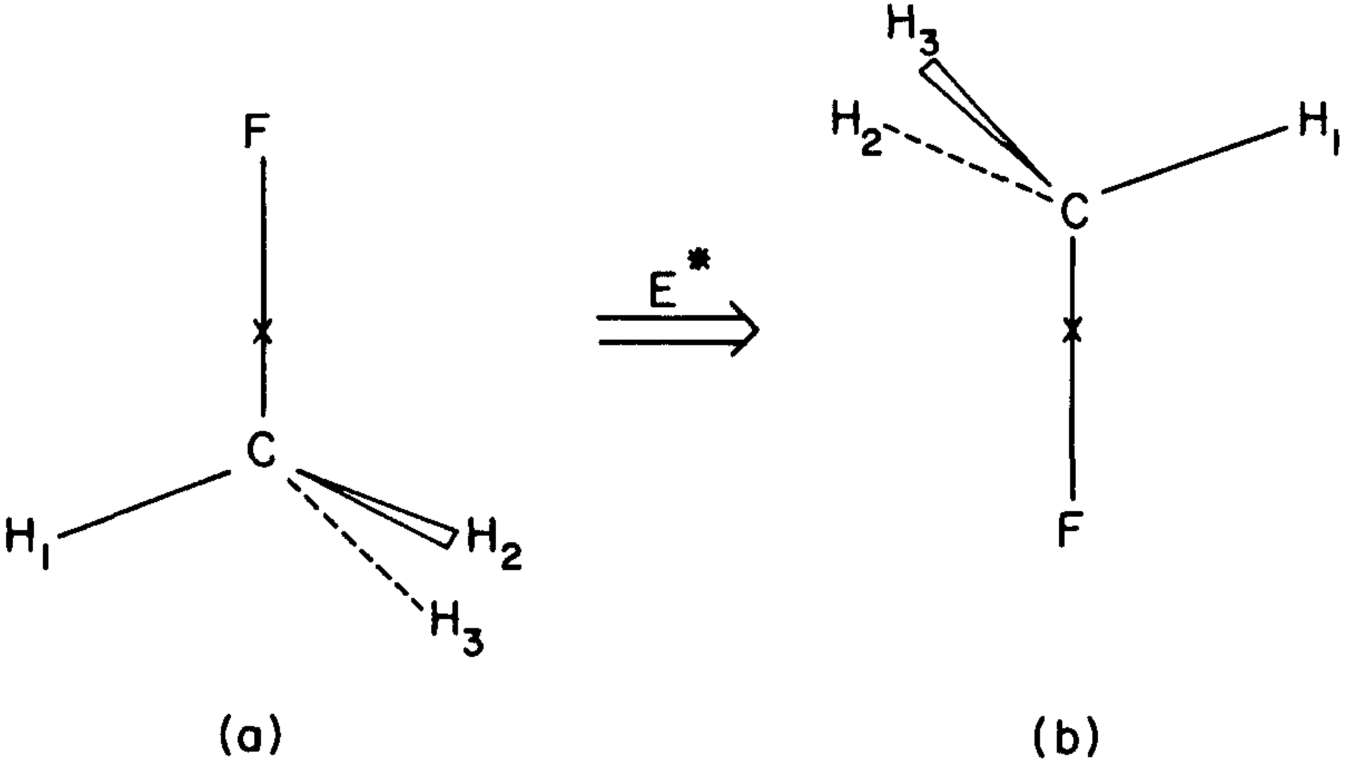
Fig. 1-3. The 12 distinct forms of an ethylene molecule in which the protons are labeled 1 to 4 and the carbon nuclei 5 to 6. Distinct forms cannot be interconverted by simply rigidly rotating them in space.

version: distinct nuclear labeled form, subgroup of CNP group

$$\{E,\ (12)(34), (13)(24)(56), (14)(23)(56)\}$$

source: P.R. Bunker, P. Jensen

Inversion group



The effect of E^* on CH_3F without drawing the space fixed axes.

inversion group: contains only two elements, *E* and *E** ;
*E** and *P* commute with each other

$$\mathcal{E} = \{E, E^*\}$$

source: P.R. Bunker, P. Jensen

CNPI groups

CNPI group: contains all possible permutations of identical nuclei with and without inversion; thus, it contains twice as many elements as the CNP group

CNPI group of ethylene, C_2H_4:

$$\boldsymbol{S}_4^{(\mathrm{H})} \otimes \boldsymbol{S}_2^{(\mathrm{C})} \otimes \mathcal{E}$$

contains 96 elements

source: P.R. Bunker, P. Jensen

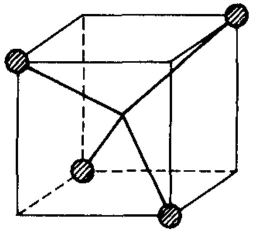
Molecular symmetry (MS) group

MS group: a convenient subgroup of the CNPI group; the group corresponding to one version of the molecule

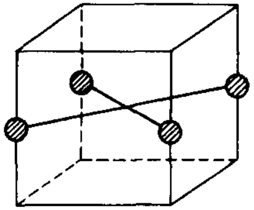
structural degeneracy: presence of more than one version of the equilibrium structure of the molecule (one cannot simply interconvert the numbered forms by simple rotations, only through a potential barrier

methane: two versions
(deform through planar form)
ethylene: 12 versions

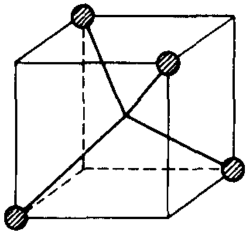
contains no *unfeasible elements* of CNPI defined for particular experiments



(a)



(b)



(c)

source: P.R. Bunker, P. Jensen

Molecular symmetry (MS) group

MS group of CH_3F (no interconversion of clockwise and anticlockwise forms: C_{3v}(M)

MS group of ethylene (no distinctions between the 12 versions: D_{2h}(M)

MS group of ammonia (with inversion tunneling): same as CNPI group, D_{3h}(M)

source: P.R. Bunker, P. Jensen

Nuclear spin statistics

Symmetry of the complete internal wavefunction Φ_{int} is restricted

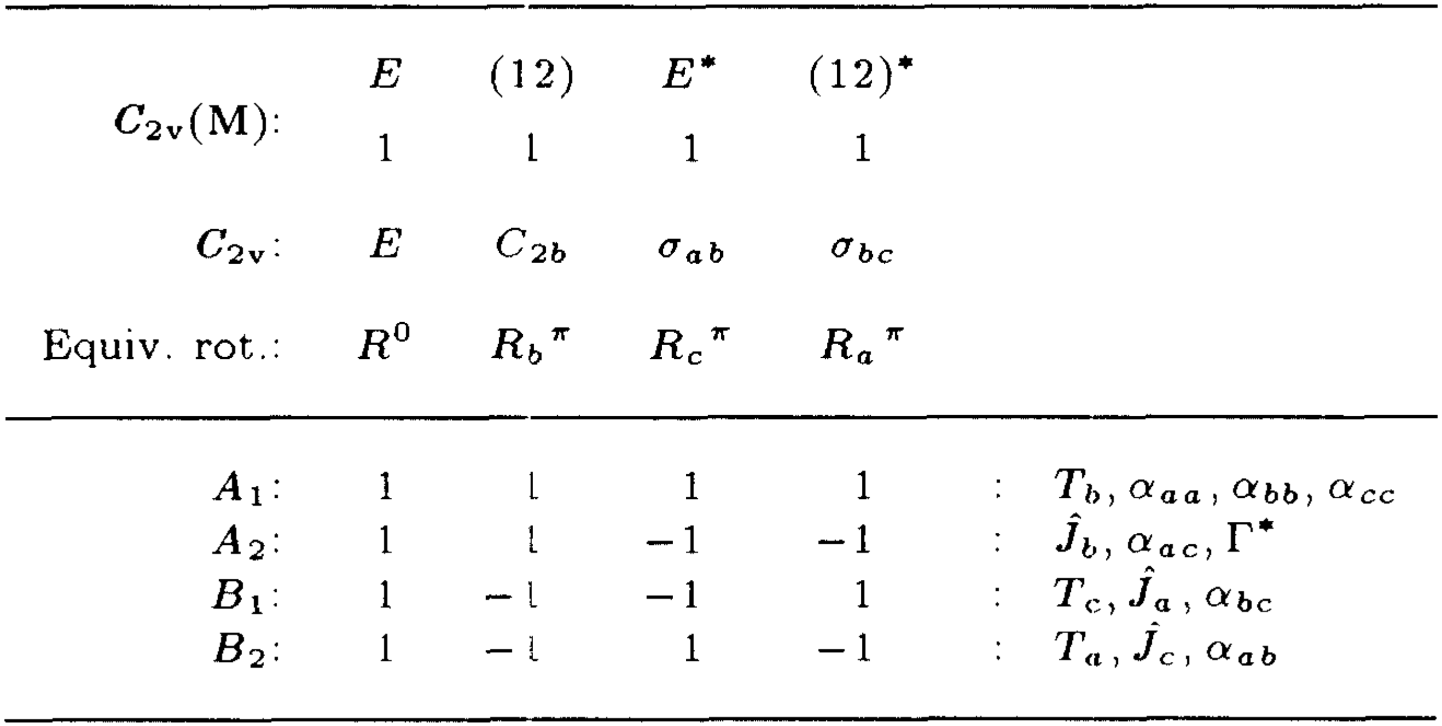
Complete internal wavefunction can have + or – parity according to the effect of E^* on it: Φ_{int} transforms as one of two nondegenerate irreducible representations of the CNPI group, usually written as Γ^+ (+ parity) and Γ^- (– parity)

A rovibronic state of Γ_{rve} symmetry can be combined with a nuclear spin state Γ_{ns} if the product of the two symmetries is allowed for Φ_{int}

The number of nuclear spin states of a given symmetry may differ for each Γ_{rve} symmetry: origin of nuclear spin statistics

Nuclear spin statistics

Example: $\mathbf{H_2{}^{16}O}$ with CNPI group C_{2v}(M)



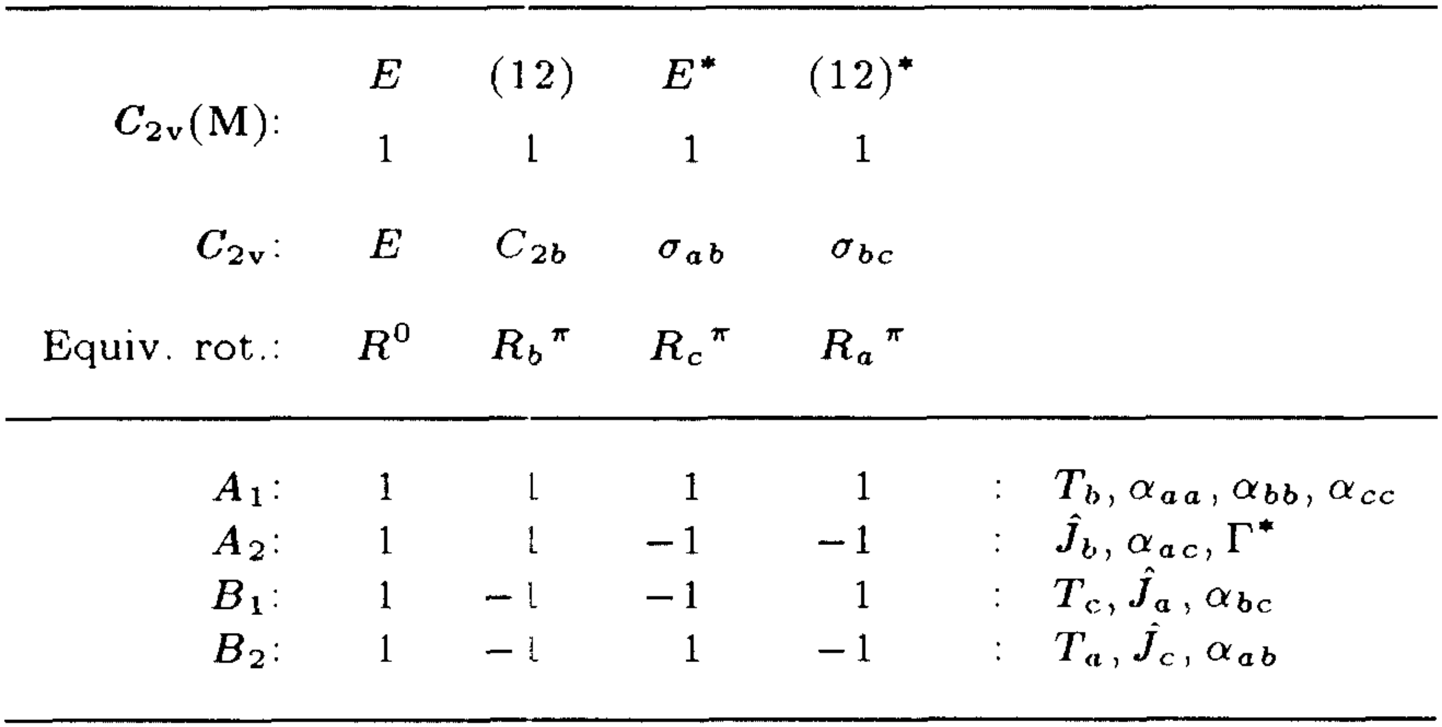
$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$		
	1	1	1	1		
C_{2v}:	E	C_{2b}	σ_{ab}	σ_{bc}		
Equiv. rot.:	R^0	$R_b{}^{\pi}$	$R_c{}^{\pi}$	$R_a{}^{\pi}$		
A_1:	1	1	1	1	:	$T_b, \alpha_{aa}, \alpha_{bb}, \alpha_{cc}$
A_2:	1	1	-1	-1	:	$\hat{J}_b, \alpha_{ac}, \Gamma^*$
B_1:	1	-1	-1	1	:	$T_c, \hat{J}_a, \alpha_{bc}$
B_2:	1	-1	1	-1	:	$T_a, \hat{J}_c, \alpha_{ab}$

(12): odd permutation of fermions (Pauli exclusion principle); changes sign of Φ_{int}: (12) $\Phi(H_2O) = -\,\Phi(H_2O)$

E^*: $\Gamma^+ = B_2$ and $\Gamma^- = B_1$

Nuclear spin statistics

Example: **$D_2{}^{16}O$** with CNPI group $C_{2v}(M)$



$C_{2v}(M)$:	E	(12)	E^*	$(12)^*$		
	1	1	1	1		
C_{2v}:	E	C_{2b}	σ_{ab}	σ_{bc}		
Equiv. rot.:	R^0	$R_b{}^{\pi}$	$R_c{}^{\pi}$	$R_a{}^{\pi}$		
A_1:	1	1	1	1	:	T_b, α_{aa}, α_{bb}, α_{cc}
A_2:	1	1	-1	-1	:	$\hat{J}_b$, α_{ac}, Γ^*
B_1:	1	-1	-1	1	:	T_c, $\hat{J}_a$, α_{bc}
B_2:	1	-1	1	-1	:	T_a, $\hat{J}_c$, α_{ab}

(12): odd permutation of bosons; does not change sign of Φ_{int}

E^*: $\Gamma^+ = A_1$ and $\Gamma^- = A_2$

Nuclear spin wavefunctions of H_2O

nucleus α having spin I_α: total no. of nuclear spin functions

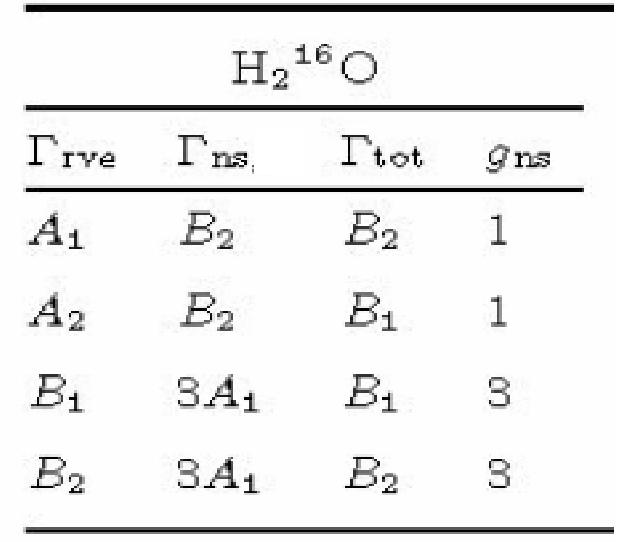
H has the spin functions: $\alpha = |½, ½\rangle$, $\beta = |½, -½\rangle$

^{16}O has the spin function: $\delta = |0,0\rangle$

possible combinations: $\alpha\,\alpha\,\delta$, $\alpha\,\beta\,\delta$, $\beta\,\alpha\,\delta$, $\beta\,\beta\,\delta$

symmetrization of $\alpha\alpha$ and $\beta\beta$ spin functions: $\Gamma_{\mathrm{ns}} = 3\,A_1 \oplus B_2$

spin functions are invariant to E^*: positive parity



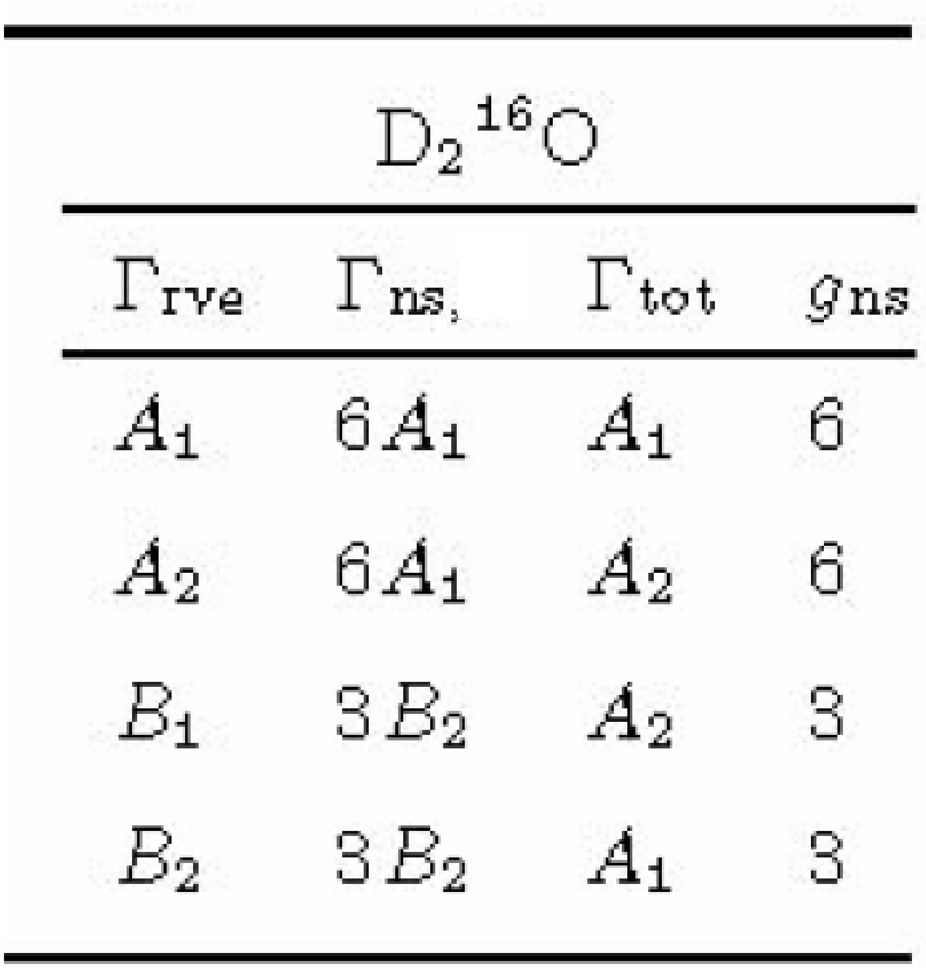
$H_2{}^{16}O$

Γ_{rve}	Γ_{ns}	Γ_{tot}	g_{ns}
A_1	B_2	B_2	1
A_2	B_2	B_1	1
B_1	$3A_1$	B_1	3
B_2	$3A_1$	B_2	3

para-$H_2{}^{16}O$

ortho-$H_2{}^{16}O$ (higher weight)

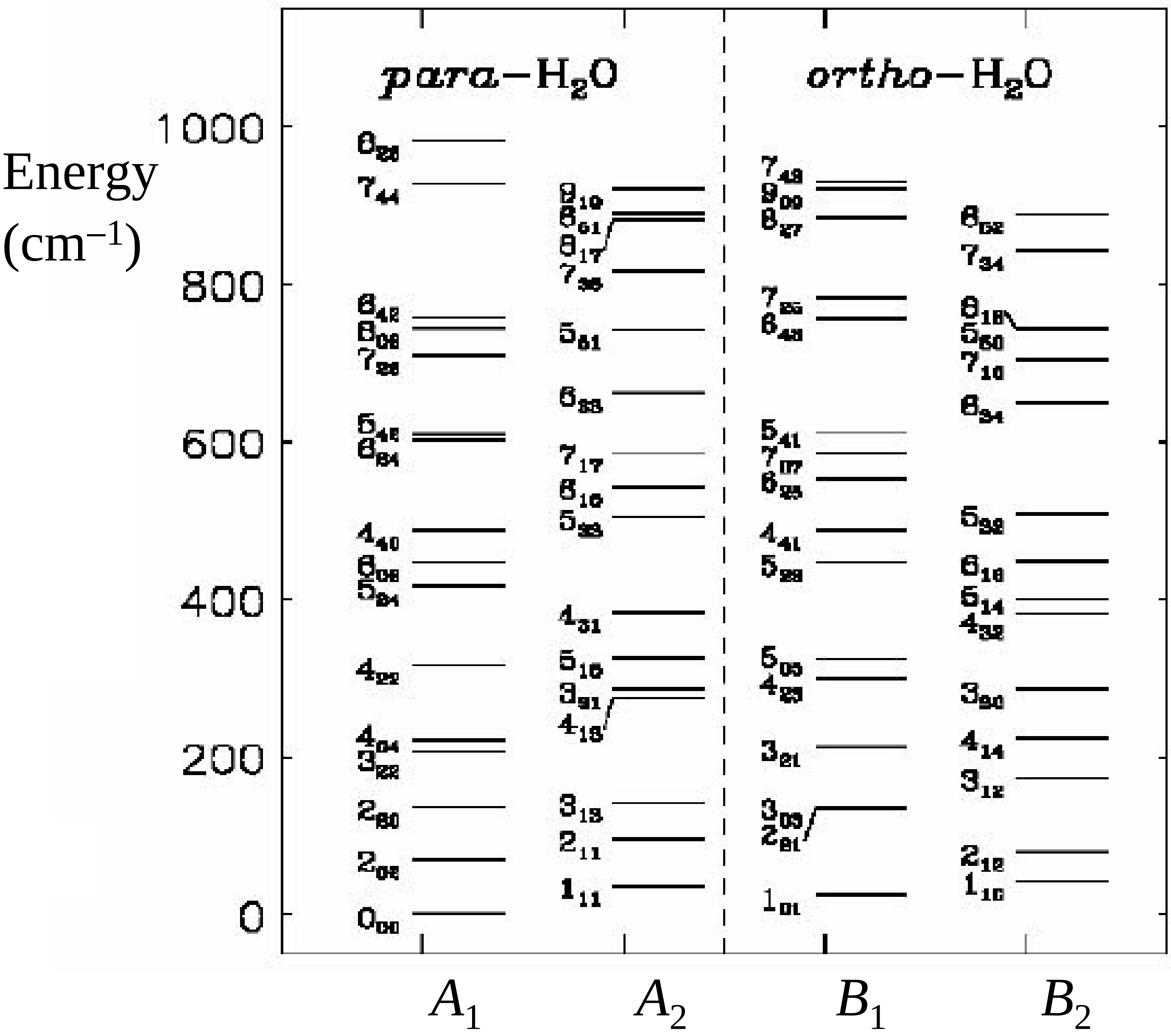
Nuclear spin wavefunctions of D_2O



$D_2{}^{16}O$

$\Gamma_{\rm rve}$	$\Gamma_{\rm ns,}$	$\Gamma_{\rm tot}$	$g_{\rm ns}$
A_1	$6\,A_1$	A_1	6
A_2	$6\,A_1$	A_2	6
B_1	$3\,B_2$	A_2	3
B_2	$3\,B_2$	A_1	3

Pure rotational energy levels of $H_2{}^{16}O$



source: P. Jensen

Nuclear spin wavefunctions of $^{14}NH_3$

nucleus α having spin I_α: total of nuclear spin functions

spin functions are invariant to E^*: positive parity

Example: $^{14}NH_3$ with MS group D_{3h}(M)

D_{3h}(M):	E	(123)	(23)	E^*	$(123)^*$	$(23)^*$		
	1	2	3	1	2	3		
D_{3h}:	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
Equiv. rot.:	R^0	$R_z^{2\pi/3}$	R_0^π	R_z^π	$R_z^{-\pi/3}$	$R_{\pi/2}^\pi$		
A_1':	1	1	1	1	1	1	:	$\alpha_{zz}, \alpha_{xx} + \alpha_{yy}$
A_1'':	1	1	1	-1	-1	-1	:	Γ^*
A_2':	1	1	-1	1	1	-1	:	$\hat{J}_z$
A_2'':	1	1	-1	-1	-1	1	:	T_z
E':	2	-1	0	2	-1	0	:	$(T_x, T_y), (\alpha_{xx} - \alpha_{yy}, \alpha_{xy})$
E'':	2	-1	0	-2	1	0	:	$(\hat{J}_x, \hat{J}_y), (\alpha_{xz}, \alpha_{yz})$

Nuclear spin wavefunctions of $^{14}\mathrm{NH}_3$

$$(m_I = 3/2): \quad \alpha\alpha\alpha = \Phi_{\mathrm{ns}}^{(1)},$$

$$(m_I = 1/2): \quad \alpha\alpha\beta = \Phi_{\mathrm{ns}}^{(2)}, \quad \alpha\beta\alpha = \Phi_{\mathrm{ns}}^{(3)}, \quad \beta\alpha\alpha = \Phi_{\mathrm{ns}}^{(4)},$$

$$(m_I = -1/2): \quad \alpha\beta\beta = \Phi_{\mathrm{ns}}^{(5)}, \quad \beta\alpha\beta = \Phi_{\mathrm{ns}}^{(6)}, \quad \beta\beta\alpha = \Phi_{\mathrm{ns}}^{(7)},$$

$$(m_I = -3/2): \quad \beta\beta\beta = \Phi_{\mathrm{ns}}^{(8)},$$

$\Phi_{\mathrm{ns}}^{(1)}$ and $\Phi_{\mathrm{ns}}^{(8)}$ are invariant to all symmetry operations

reducible representation for m_I = ½ or –½ :

E	(123)	(23)	E^*	$(123)^*$	$(23)^*$
3	0	1	3	0	1

irreducible representation for m_I = ½ or –½ : $A_1{}' \oplus E'$

altogether we have: $4A_1{}' \oplus 2E'$

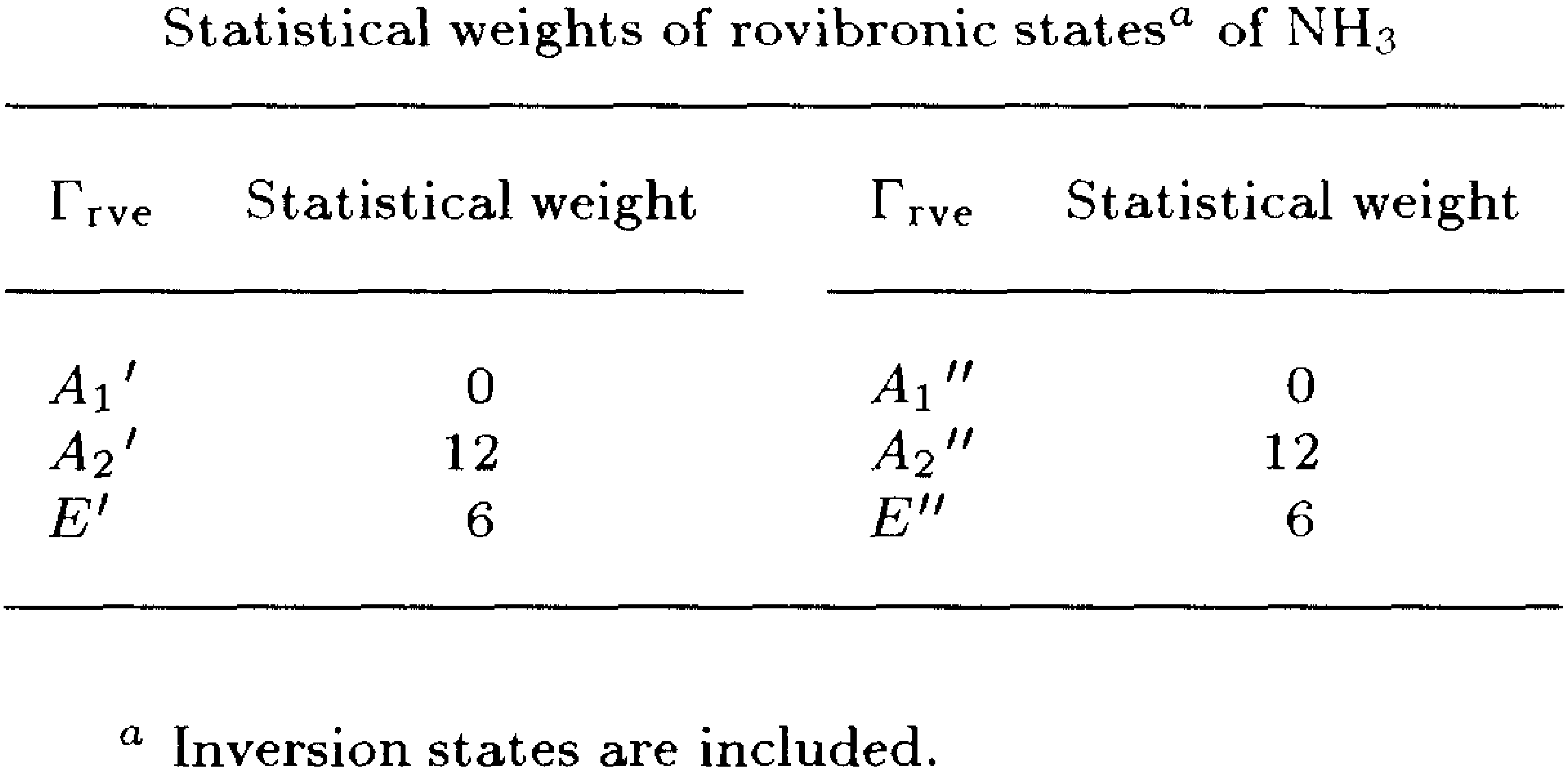
^{14}N nucleus three spin functions, altogether 24:

$$\boxed{\Gamma_{\mathrm{nspin}}^{\mathrm{tot}} = 12A_1{}' \oplus 6E'}$$

Spin statistical weights

(23): odd permutation of fermions; changes sign of Φ_{int}

E^*: $\Gamma^+ = A'_2$ and $\Gamma^- = A''_2$ is symmetry of Φ_{int}

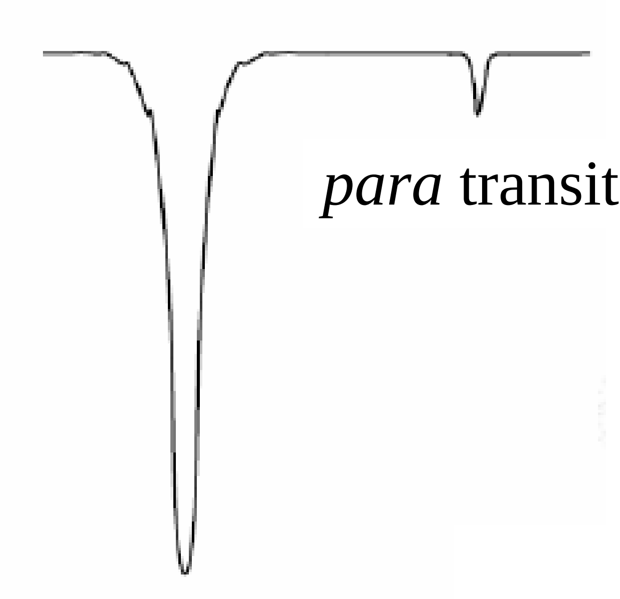


Statistical weights of rovibronic states[a] of NH_3

Γ_{rve}	Statistical weight	Γ_{rve}	Statistical weight
A_1'	0	A_1''	0
A_2'	12	A_2''	12
E'	6	E''	6

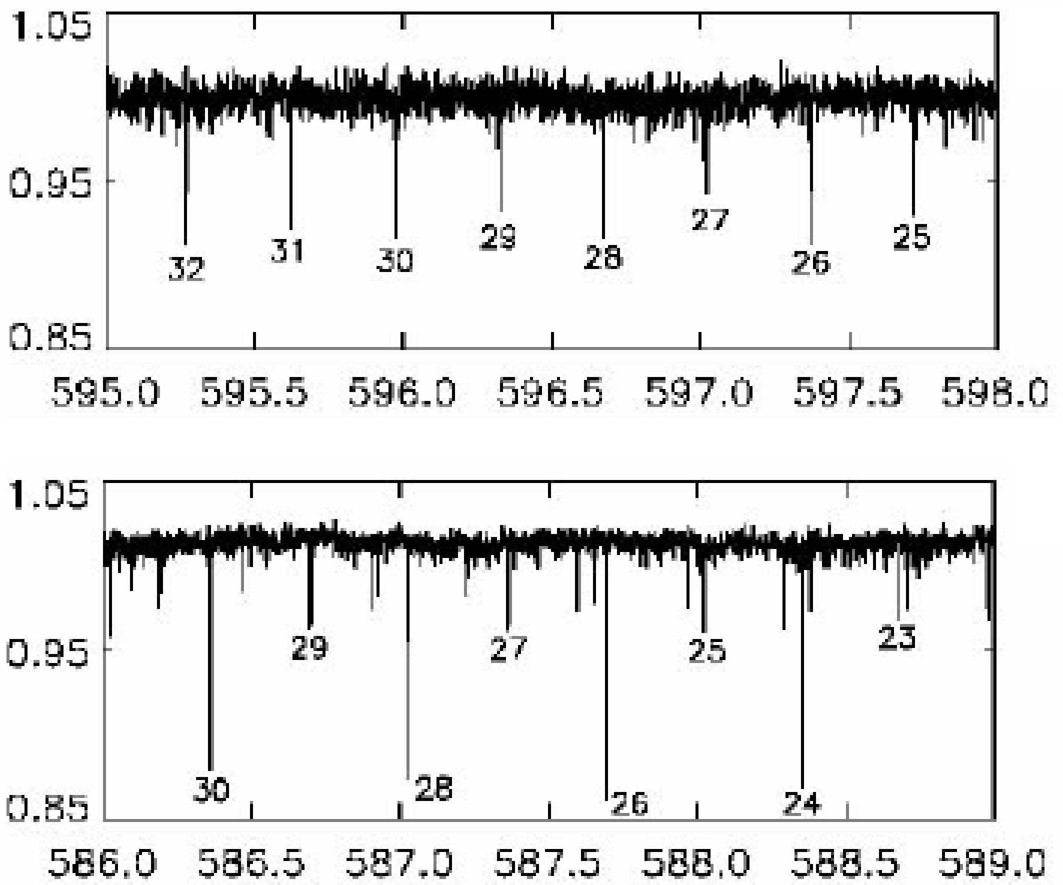
[a] Inversion states are included.

Effect of spin statistical weights on observed spectra: intensity alterations



para transition

ortho transitions



Ortho-para interaction?

The molecular Hamiltonian may contain the so far neglected interaction terms between angular momenta, leading to hyperfine interactions which can couple ortho and para levels

$$\begin{bmatrix} H_{\mathrm{oo}} & H_{\mathrm{op}} \\ H_{\mathrm{po}} & H_{\mathrm{pp}} \end{bmatrix}$$

$$H_{qq} = E_{\mathrm{rve},q} + \langle \Phi_q | \hat{H}_{\mathrm{hfs}} | \Phi_q \rangle$$

$$H_{\mathrm{po}} = H_{\mathrm{op}} = \langle \Phi_{\mathrm{p}} | \hat{H}_{\mathrm{hfs}} | \Phi_{\mathrm{o}} \rangle$$

source: P. Jensen

Research into symmetry breaking

- Due to weak interaction forces in nuclei E^* is not a universal symmetry operation, P violation was already observed in atoms, its detection is under way in molecules: parity violation studies, energy difference in enantiomers
- Is permutation symmetry universal? Can one observe the missing transitions?
- Etc.