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NOTATIONS AND CONVENTIONS IN MOLECULAR SPECTROSCOPY: PART 2. SYMMETRY NOTATION

(IUPAC Recommendations 1997)

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Notations and conventions in molecular spectroscopy: Part 2. Symmetry notation (IUPAC Recommendations 1997)

Abstract -- The field of *Molecular Spectroscopy* was surveyed in order to determine a set of conventions and symbols which are in common use in the spectroscopic literature. This document, which is *Part 2* in a series, establishes the notations and conventions used for the description of *symmetry* in rigid molecules, using the Schoenflies notation. It deals firstly with the *symmetry operators* of the molecular point groups (also drawing attention to the difference between symmetry operators and elements). The conventions and notations of the *molecular point groups* are then established, followed by those of the *representations* of these groups as used in molecular spectroscopy. Further parts will follow, dealing *inter alia* with *permutation* and *permutation-inversion symmetry notation*, *vibration-rotation spectroscopy* and *electronic spectroscopy*.

PREAMBLE

The sub-committee on Notations and Conventions in Molecular Spectroscopy was initiated by Commission I.5, the Commission on Molecular Structure and Spectroscopy, to establish and recommend a set of conventions and symbols from those that are in common use in the spectroscopic literature.

Part 1 of the series is titled *General Spectroscopic Notation* [1]. The present part deals with symmetry notation referring to point groups, and the recommendations follow those of Jenkins [2], Mulliken [3], IUPAP [4], and IUPAC [5] in the main. The notation of Herzberg [6] is recommended when it differs from that of Wilson, Decius and Cross [7]. It is pointed out that the International Union of Crystallography uses another approach [8].

Part 2. SYMMETRY NOTATION

- 2.1 Symmetry Operators for the Molecular Point Groups
- 2.2 The Molecular Point Groups
- 2.3 Representations for Molecular Point Groups and Spectroscopy

Symbols used in this paper

Greek Alphabet			
Γ	2.3.1; 2.3.3c	Σ, σ	2.3.3a
$\Gamma_j^{(\alpha)}$	2.3.2	σ	2.1.2a
Γ, γ	2.3.3c	σ_h	2.1.2b
Δ, δ	2.3.3c	σ_v, σ_v'	2.1.2c
Π, π	2.3.3c	σ_d, σ_d'	2.1.2d; 2.1.7
Φ, ϕ	2.3.3c	$\sigma_{xy}, \sigma(x,y)$	2.1.6
Ω	2.3.11		

Symbols			
matrices	2.2.17	1, 2	2.3.6; 2.3.9; 2.3.12a
' , ''	2.1.7; 2.3.7	+ -	2.3.13
upper/lower case	2.3.4		
Latin Alphabet and Numbers			
A	2.3.3a; 2.3.12	G	2.3.3e; 2.3.12
a	2.3.3a	g	2.3.3e; 2.3.5a
B	2.3.3b; 2.3.12	H, h	2.3.3f
b	2.3.3b	I, I	2.1.1; 2.3.12
C_n, C_n^1	2.1.3; 2.2.1	I_h	2.2.13
$C_n^k, C_n^k(x)$	2.1.3; 2.1.6	i	2.1.5
C_2, C_2', C_2''	2.1.7	ℓ	2.3.8
C_i	2.2.2	m	2.3.10
C_{nv}	2.2.6	O	2.2.11
C_{nh}, C_{1h}	2.2.7	O_h	2.2.12
C_s	2.2.7	S_n, S_n^1	2.1.4
$C_\infty(\phi)$	2.1.3	$S_\infty(\phi)$	2.1.4
$C_{\infty v}$	2.2.14	S_n^k, S_2^1	2.1.4; 2.1.5
D_n, D_2	2.2.3	S_{2n}, S_2	2.2.2
D_{nh}, D_{2h}	2.2.4	T, T	2.2.8; 2.3.3d
D_{nd}, D_{2d}	2.2.5	T_d	2.2.10
$D_{\infty h}$	2.2.15	T_h	2.2.9
E, E	2.1.1; 2.3.3c; 2.3.12	t	2.3.3d
e, e	2.1.1; 2.3.3c	u	2.3.5b
F	2.3.3d; 2.3.12	x, y, z	2.1.6
f	2.3.3d		

Typographical Conventions:

It is desirable to distinguish by means of typographic conventions between the *symmetry elements* of a body (such as, for example, the invariant line called a rotation axis) and the *symmetry operators* (sometimes called symmetry operations) which bring a body into coincidence with itself and which form a *point group*. Unfortunately there seems to be no established set of typographic conventions for doing so. The conventions used in this paper are stated below. It is recommended that authors who do not follow these conventions clearly define their own conventions.

Symbols for symmetry operators are printed italic, with sub- and super-scripts that are upright except for the variables k and n which are replaced by numbers for a specific operator [5]. Following Donnay (*Acta Cryst. A28*, (1972) 110), the power of an operator, k , is specified even when it is one, e.g., C_n^1 is used instead of C_n ; and S_n^1 is used instead of S_n .

Symbols for symmetry elements are seldom used in this document. Those that are included are printed upright.

Symbols for symmetry groups are printed italic with upright subscripts, following common usage.

Symbols for irreducible representations of point groups, which are usually called symmetry species in spectroscopy, are printed upright. Subscripts are upright except when they are the variables j or α which are replaced by numbers in specific cases. Γ is printed italic when it is a variable to be replaced by other symbols in specific cases.

2.1 SYMMETRY OPERATORS OF THE MOLECULAR POINT GROUPS

The symbols for *symmetry operators* are defined below. Only the Schoenflies notation is followed here. The operator symbols approved by the International Union of Crystallography [8] for use in crystal chemistry, which include translational symmetry operators, differ from those given here.

The correspondences are ($E \equiv I$), ($C_n^1 \equiv n$) ($i \equiv \bar{I}$), ($\sigma \equiv m$), ($S_n^1 \equiv \bar{n}$ or \bar{X});. A table showing the alternative notations of the point groups used by crystallographers is found in Ref. 8, p. 801, as well as in Schutte [9], p. 393.

2.1.1	Identity operator	$E; e; I$
2.1.2	Reflection operator for reflection across a plane	
	(a) across a general plane	σ
	(b) across a horizontal plane	σ_h
	(c) across a vertical plane	σ_v
	(d) in a plane bisecting two C_2 -axes which are perpendicular to the principal C_n axis	σ_d
2.1.3	n -fold rotation operator for k successive rotations through an angle of $2\pi/n$ about an n -fold rotation axis, where $n = 2, 3, \dots$; $k = 1, 2, \dots, n - 1$	$C_n^k; C_n^1 = C_n$
	or: $n = \infty$; rotation through an arbitrary angle ϕ	$C_\infty(\phi)$

- 2.1.4 n -fold rotation-reflection (alternating; improper) operator for k successive rotation-reflections about an n -fold rotation-reflection axis for a rotation through an angle of $2\pi/n$ followed by a reflection in a plane perpendicular to the axis, where $n = 2, 3, 4, \dots$; $k = 1, 2, \dots (n-1)$ $S_n^k; S_n^1 = S_n$
 or: $n = \infty$; rotation through an arbitrary angle ϕ $S_\infty(\phi)$
- 2.1.5 Inversion operator through the centre of symmetry i , note $S_2^1 \equiv i$
- 2.1.6 Specification of orientation: If it is needed to specify the orientation of the symmetry element with respect to a molecule-fixed set of cartesian axes (x, y, z) which is involved in the symmetry operation, an appropriate subscript or symbols in brackets may be added to the symbol of the symmetry operation, e.g., σ_{xy} , $\sigma(x, y)$, $C_n^k(x)$
- 2.1.7 Distinguishing between same kind of operators: symmetry operators of the same kind, but belonging to different group classes must be distinguished by consecutive right accent superscripts, e.g., C_2 , C_2' , C_2'' , and σ_d and σ_d' in D_{4h}

2.2 THE MOLECULAR POINT GROUPS

The essential operators in each point group are listed. Other operators are present in the groups marked **, required by the presence of those listed. References 6 and 7 give a complete listing of the operators in each group.

- 2.2.1 Finite rotation groups having only C_n^k operators C_n
- 2.2.2 Rotation-reflection groups having only S_{2n}^k operators $S_{2n}; S_2 \equiv C_i$
- 2.2.3 Group of operators of the group C_n plus n -dihedral C_2 operators $D_n; D_2$
- 2.2.4 Group of operators of the group D_n plus the σ_h operator** $D_{nh}; D_{2h}$
- 2.2.5 Group of operators of the group D_n plus $n\sigma_d$ operators** $D_{nd}; D_{2d}$
- 2.2.6 Group of operators of the group C_n plus $n\sigma_v$ operators C_{nv}
- 2.2.7 Group of operators of the group of C_n plus the σ_h operator** $C_{nh}; C_{1h} \equiv C_s$
- 2.2.8 Group of rotation operators of a tetrahedron T
- 2.2.9 Group of operators of T plus the inversion operator i T_h
- 2.2.10 Full group of operators of a tetrahedron T_d
- 2.2.11 Group of operators for the rotations of an octahedron (isomorphous with T_d) O
- 2.2.12 Full group of operators of an octahedron (Group of operators of O plus the inversion operator i) O_h

- 2.2.13 Full group of operators for an icosahedron I_h
- 2.2.14 Group of operators for an asymmetric linear molecule $C_{\infty v}$
- 2.2.15 Group of operators for a symmetric linear molecule (the group of operators of $C_{\infty v}$ plus the inversion operator i)** $D_{\infty h}$
- 2.2.16 Alternative definitions: Some of the point groups may be defined in an alternative fashion as direct product groups with the i -operator, e.g., for n odd $C_n \times i = S_{2n}$. The C_{nh} groups are also generated by $C_n \times \sigma_h = C_{nh}$ or for n even by $C_n \times i = C_{nh}$
- 2.2.17 Matrices representing symmetry operators: the matrices representing the symmetry operators of a group G are indicated by the corresponding heavy-print symbols. Definitions should include whether the operators are active (operating on the position vectors) or passive (operating on the molecule-fixed coordinate system), whether the rotations are clockwise or anticlockwise with respect to the positive direction of the rotation axis, and the handedness of the axial system.

2.3 REPRESENTATIONS FOR MOLECULAR POINT GROUPS AND SPECTROSCOPY

- 2.3.1 Reducible representation of group G Γ
- 2.3.2 Irreducible representations of group G , where $j = 1, 2, 3, \dots$ numbers the representations sequentially and $(\alpha) = 1, 2, 3$ indicates the dimension of each representation $\Gamma_j^{(\alpha)}$
- alternatively, the symbols of 2.3.3 may replace $\Gamma_j^{(\alpha)}$ A_{1g}, F_{2u} , etc.
- 2.3.3 The dimensions of the representations are indicated by the following symbols (which may be sub- and superscripted according to 2.3.5 - 2.3.12), the choice between upper case and lower case letters being regulated by 2.3.4:
- | | <u>polyatomic</u> | <u>linear</u> |
|--|-------------------|--|
| (a) one-dimensional, symmetric (+1) with respect to the primary operator C_n^1 or S_n^1 of the point group | A, a | Σ, σ |
| (b) one-dimensional, antisymmetric (-1) with respect to the primary operator C_n^1 or S_n^1 of the point group | B, b | - - |
| (c) two-dimensional and pseudo two-dimensional | E, e | Π, π
Δ, δ
Φ, ϕ
Γ, γ |

Note: The complex conjugate one-dimensional representations Γ_i and Γ_j are bracketed together in spectroscopy as a pseudo E-representation or corepresentation, because the Hamiltonian is invariant to the operator which expresses time-reversal, that is, the wavefunction and its complex conjugate yield the same energy. This occurs, for instance, in the groups C_n, S_{2n} , and C_{nh}

- (d) three-dimensional (the symbol T is customarily used in the context of inorganic complexes, to avoid confusion with F for atomic states in the full rotation group) F, f; T, t
- (e) four-dimensional G, g
- (f) five-dimensional H, h
- 2.3.4 Symbols for symmetry species in 2.3.3 are used upper case or lower case as follows:
- (a) Individual normal vibration wavefunction lower case
- (b) Overall vibrational state wavefunction upper case
- (c) Individual one-electron (orbital) wavefunction lower case
- (d) Overall electronic state wavefunction upper case
- (e) Overall vibronic state wavefunction upper case
- 2.3.5 Right subscripts on the representations of 2.3.3 with respect to the inversion operator i :
- (a) representations which are symmetric (+1) with respect to the inversion operator i g
- (b) representations which are antisymmetric (-1) with respect to the inversion operator i u
- 2.3.6 Right subscripts on the representations A and/or B of 2.3.3 for the groups D_n , D_{nh} and D_{nd} or for C_{nv}
- (a) representations which are symmetric with respect to the C_2' operator for a rotation around a C_2' axis \perp to the generating axis C_n of the groups D_n , D_{nh} , and D_{nd} 1
- (b) representations which are symmetric with respect to the σ_v operator in the group C_{nv} 1
- (c) representations which are antisymmetric with respect to the C_2' operator in the groups D_n , D_{nh} , and D_{nd} 2
- (d) representations which are antisymmetric with respect to the σ_v operator in the groups C_{nv} 2
- Note:** To resolve the ambiguity in assigning the subscript labels of the B species of the point groups C_{2v} and D_{2h} for planar molecules, the x axis must be chosen perpendicular to the plane of the molecule. For D_{2h} the z axis is chosen so that it passes through the largest number of atoms or, if this is not unique, then so that it cuts the largest number of bonds [3]. The Mulliken [3] numbering of the B_1 , B_2 and B_3 species of D_{2h} is followed.
- 2.3.7 Right superscripts on the representations of 2.3.3 with respect to the σ_h operator
- (a) representations which are symmetric with respect to the σ_h -operator ,
- (b) representations which are antisymmetric with respect to the σ_h -operator "

- 2.3.8 Right subscript ℓ on the E-representation where $\ell = 1, 2, 3, \dots$
 $(\frac{1}{2}n - 1)$ for n even and $\frac{1}{2}(n - 1)$ for n odd, where n is the
order of the generating operator of the point group ℓ
- 2.3.9 Right subscripts 1 and 2 on F-representations of the groups
 T_d, O, O_h 1, 2
Note: Since the use of 1 or 2 is arbitrary, the notation of
Herzberg [6] and Wilson, Decius and Cross [7] is recommended
- 2.3.10 A left superscript m to indicate electron spin multiplicity
 $m = 2S + 1$ may be added to the species symbols of 2.3.4(d)
and (e); for example, $^3A_2, ^3\Sigma_g^-$ m
- 2.3.11 A right subscript Ω or P of 1.2.2.16 [1] may be added to the
species symbols of linear molecules, for example, $^2\Pi_{(3/2)u}, ^2\Delta_{5/2}$ Ω
- 2.3.12 Level designations according to the value of Ω for
very strong spin-orbit coupling (Hund's case c):
- (a) diatomic and linear molecules
- odd electron states* $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \dots$
- even electron states* $0^+, 0^-, 1, 2, \dots$
- (b) non-linear molecules
- odd electron states**+ $E_{1/2}, E_{3/2}, \dots, G_{5/2}, I_{5/2}, \dots$
- even electron states**+ $A_1, A_2, B_1, B_2, E_1, E_2, F_1, \dots$
- 2.3.13 Right superscripts on the Σ representations of the groups
 $C_{\infty v}$ and $D_{\infty h}$
- (a) representations which are symmetric with
respect to the reflection operator σ_v +
- (b) representations which are antisymmetric
with respect to the reflection operator σ_v -

*For $D_{\infty h}$ add the g, u subscripts.

**For D_{6h} and O_h add the g, u subscripts, and for D_{3h} and C_{3h} add the ' and '' superscripts, omitting the 1 and 2 subscripts.

+Multiply the orbital symmetry species by the spin symmetry species to obtain the appropriate level designation, keeping in mind the ' and '' signs, as well as g and u.

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