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THE INTERSECTION THEOREM AND THE CORRELATION METHOD

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THE INTERSECTION THEOREM AND THE CORRELATION METHOD

by

JANET PIERCE

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Abstract

THE INTERSECTION THEOREM AND THE CORRELATION METHOD

by

Janet Pierce

Adviser: Professor Louis Massa

The Intersection Theorem and the Correlation Method each provide for the handling of symmetry data involving a system and its subsystems. The Intersection Theorem makes a statement about the overall minimum symmetry of a composite system, while the Correlation Method translates symmetry information about the parts of the system into the framework of the complete molecule. In both cases, the necessary information or resulting symmetry data can be obtained by other methods, but comparisons involving tensor properties of crystals and molecular orbitals of isolated molecules will show that standard methods are more time-consuming and less conceptually satisfying for composite systems.

ACKNOWLEDGEMENT

For the development and preparation of this dissertation, I wish to express my deep appreciation to my thesis advisor, Louis Massa, and to the members of my committee, Vojtech Fried and Joseph Dannenberg. Dr. Massa's interest in the topic of composite symmetry, along with the work of J.A. McMillan, sparked the initiation and extension of our study of combined systems. Without Dr. Massa's patience, support, and guidance, these researches might never have reached a conclusion. The perceptive criticism of Drs. Dannenberg and Fried sharpened and clarified the concepts expressed and suggested fruitful directions for investigation.

Finally, I thank my husband, David, both for his help in compiling tables and checking the manuscript and for his unfailing love and understanding.

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I. INTRODUCTION

The Role of Symmetry in the Description of Composite Systems

Experimental chemistry involves not only observing and measuring chemical compounds and their reactions, but also fitting these observations into a framework of theory. The study of symmetry and of symmetry changes through the theory of groups has in particular aided in the interpretation of experimental data and in the design of new experiments. Since the symmetry of the molecule or crystal determines the number and variety of energy levels it may possess, symmetry considerations alone limit the pathways to be explored in many chemical problems.

The Intersection Theorem and the Correlation Method each provide for the handling of symmetry data involving a system and its subsystems. The Intersection Theorem makes a statement about the overall minimum symmetry of a composite system, while the Correlation Method translates symmetry information about the component parts of the system into the framework of the complete molecule or crystal. In both cases, the necessary information or resulting symmetry data can be obtained by other methods, but comparisons will show that standard methods are more time-consuming and less satisfying conceptually for composite systems.

The Intersection Theorem was stated by J.A.McMillan[1] in a limited form applying to a crystal in a tensor field:

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[1] J.A. McMillan, Amer. J. Phys. 37, no. 8, p. 793

> An experiment in which a crystal of symmetry point group G is in a uniform tensor field of symmetry point group G' has the symmetry of the intersection of G and G', i.e.,
>
> $$G'' = G \cap G'$$

The application of the theorem was further limited to the treatment of equilibrium properties of crystals as an alternate method of determining the form of invariant tensors under the symmetry operations of the crystallographic point group. This involves a large class of applications whose results are well known.[2]

Attempts to completely generalize the theorem as a method of determining the symmetry of an arbitrary composite system when the symmetry and orientation of the component parts are known led to difficulties immediately: the symmetry of the whole may be greater than that of its parts. Development of a generalized proof, based on perturbation theory, showed that the intersection symmetry is the minimum symmetry for the composite system and clarified the conditions under which greater symmetry will be found.

While applying the Intersection to the molecular orbitals and vibrations of composite systems, the Correlation Method[3] was employed in finding the symmetry classification of normal modes and orbitals. The method involves considering

---

[2] J.F. Nye, *Physical Properties of Crystals*

[3] W.G. Fateley, et. al., *Infrared and Raman Selection Rules for Molecules and Lattice Vibrations: The Correlation Method*.

the site symmetry of individual atoms, choosing a basis set of atomic orbitals or vectors, and correlating the resulting representation in the site symmetry to the overall symmetry of the molecule or crystal by means of correlation tables for the point groups and their subgroups. Since the appropriate representation in the site group for translation vectors or for s, p, and d orbitals is available by inspection in the character tables, and the appropriate correlations are already determined and collected in the correlation tables, the time-consuming process of determining the symmetry classifications of a basis set by performing the operations of the group on the set and reducing the resulting group representation is avoided.

Both the Intersection Theorem and the Correlation Method find application in the composition and decomposition of systems, focusing attention on the significance of the symmetry of the parts in relation to the whole, thus aiding in the understanding of symmetry properties.

II. THEOREM OF GROUP INTERSECTION

Proof

J.A. McMillan stated the Theorem of Group Intersection in terms of the symmetry of an experiment involving a crystal in a tensor field[4],

$$G'' = G \cap G' \qquad \text{(II.1)}$$

where G is the symmetry of the crystal, G' of the tensor field, and G" of the composite experiment. We suggest a proof of this theorem based on perturbation theory which would extend its application to the symmetry of any two combined systems.

The Intersection Theorem may be rephrased as follows: Let Physical systems A, $\underline{A}$ have point groups $G(A)$, $G(\underline{A})$ with elements $O(A)$, $O(\underline{A})$. The operations $O(A)$ act only on the coordinates of system A, while the operations $O(\underline{A})$ act only on those of $\underline{A}$. Form a composite system $A\underline{A}$ in such fashion that the invariant points of $G(A)$ and $G(\underline{A})$ coincide, and the position of symmetry planes is specified. Now consider the groups $G'(A)$ and $G'(\underline{A})$, isomorphic to $G(A)$ and $G(\underline{A})$ respectively, but acting on the composite system $A\underline{A}$. If no symmetry operations exist which interchange the elements of A and $\underline{A}$ then the point group $G(A\underline{A})$ of the composite system is the intersection group of $G'(A)$ and $G'(\underline{A})$:

$$G(A\underline{A}) = G'(A) \cap G'(\underline{A}) \qquad \text{(II.2)}$$

---

[4] J.A. McMillan, op. cit.

Here we point out that the Intersection Theorem may be understood from the point of view of the perturbation theory of coupled systems.[5] Suppose systems A, $\underline{A}$ to have Hamiltonians H(A), H($\underline{A}$) invariant under point groups G(A), G($\underline{A}$) respectively. Form a composite system A$\underline{A}$ so that the invariant points of G(A) and G($\underline{A}$) coincide. At first consider A and $\underline{A}$ to be dynamically independent with separable Hamiltonians:

$$H(A\underline{A}) = H(A) + H(\underline{A}) \qquad (II.3)$$

As long as the systems are uncoupled, a direct product may be formed. A group G is said to be the direct product of its subgroups G(1), G(2),...G(n) if:[6]

(1) the elements of the different subgroups commute

(2) every element g of G is expressible in one and only one way as $g = g(1)g(2)g(3)\ldots g(n)$, where g(1) is in G(1), etc.

Symbolically: $G = G(1) \times G(2) \times \cdots \times G(n) \qquad (II.4)$

From requirements (1) and (2) it follows that the subgroups have only the identity in common. Since G(A) and G($\underline{A}$) affect different coordinate systems, it follows that they have only the identity in common and the operations of G(A) commute with those of G($\underline{A}$). H(A$\underline{A}$) is then invariant under the direct product group:[7]

$$G(A\underline{A})\ \text{uncoupled} = G(A) \times G(\underline{A}) \qquad (II.5)$$

---

[5] H. Weyl, *The Theory of Groups and Quantum Mechanics*, p.93.
[6] M. Hall, *The Theory of Groups*, p.32
[7] H. Weyl, *op. cit.*

where the operations of $G(A\underline{A})$ consist of all possible ordered pairs $\{O(A), O(\underline{A})\}$. This corresponds to an alternate definition of the direct product:[8]

> Given two subgroups A and B, we may form the set of ordered pairs (a,b); $a \in A$, $b \in B$. These ordered pairs will be the elements of a new group, the direct product group $A \times B$ if we define our product by the rule
> $(a_1,b_1)(a_2,b_2) = (a_1a_2, b_1b_2)$
> Note isomorphisms: $a \longrightarrow (a, E)$
> $b \longrightarrow (b, E)$
> where the sets (a,E) and (b,E) are subgroups of the direct product. If we identify A and B with these subgroups, we can say $G = A \times B$.

Now couple the systems together with a perturbation V, which is a function of the distance between points in the two systems:

$$H(A\underline{A}) = H(A) + H(\underline{A}) + V \qquad \text{(II.6)}$$

The effect of the perturbation is to reduce the symmetry of the system to that of a subgroup of the direct product group. Not every element $R(A), S(\underline{A})$ of the direct product group will leave the intersystem distances (and therefore V) unchanged, but only those elements $\{R(A), R(\underline{A})\}$ which subject both elements to the same geometric operation. But this particular set of elements $\{R(A), R(\underline{A})\}$ forms a subgroup of the direct product which is isomorphic to the intersection group $G'(A) \cap G'(\underline{A})$, as was to have been proven. All elements of the intersection group must be elements of the composite symmetry group:

$$G(A\underline{A}) \supseteq G'(A) \cap G'(\underline{A}) \qquad \text{(II.7)}$$

[8] E.P. Wigner, Group Theory, p.171.

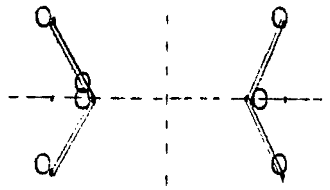
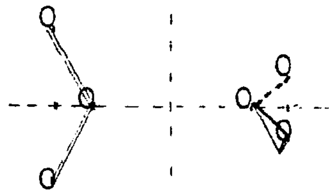
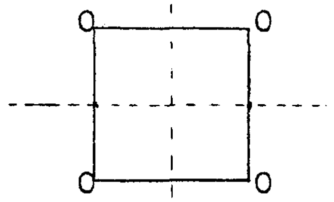
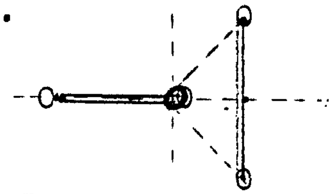
However, additional symmetry elements may exist which also preserve the intersystem distances in the case of two systems of like composition. Then a set of operations rotating, reflecting or inverting system A into system $\underline{A}$, called the interchange complex, I, increases the symmetry of the composite group. Any element of the composite group is either an element of the interchange complex or of the intersection group, since an element of the composite group either interchanges the two systems or does not. If it does, it is by definition a member of the interchange complex. If it does not, it can be regarded as acting on each of the systems separately, so taht it is a member of each original group, and hence of the intersection group.

The additional symmetry elements in the interchange complex are of two general categories:

1. Improper axes of rotation
   a. horizontal mirror plane ($=S_1$)
   b. inversion point ($=S_2$)
   c. S_{2n} axis may be generated if $C_n \in (G'(A) \cap G'(\underline{A}))$
2. Proper axes of rotation not colinear with z
   a. set of n perpendicular C_2 axes may be generated if $C_n \in (G'(A) \cap G'(\underline{A}))$
   b. perpendicular axes of higher order and mirror planes containing them
   c. non-perpendicular C_n axis

2b. and 2c. can occur only at one specific separation along the z axis, but are of particular interest since examples include transition states and systems that have non-identical molecules as components.

Figure I - Examples of Interchange Complexes

	A ¦ $\underline{A}$	$G(A\underline{A})$	$G'(A)$ $G'(\underline{A})$	I
1.		D_{2h}	$C_{2v} \cap C_{2v} = C_{2v}$	$C_2(x), C_2(y), i,$ $\sigma(xy)$
2.		D_{2d}	$C_{2v} \cap C_{2v} = C_{2v}$	$S_4, S_4^3, 2C_2'$
3.		D_{4h}	$C^*_{2v} \cap C^*_{2v} = C_{2v}$	$C_4, C_4^3, C_2, C_2',$ $2C_2'', i, S_4, S_4^3,$ $2\sigma_d$
4.		D_{3h}	$C_{\infty v} \cap C^*_{2v} = C_{2v}$	$C_3, C_3^2, S_3, S_3^5,$ $2C_2, 2\sigma_v$

* In examples 3 and 4, the invariant points of systems A and $\underline{A}$ do not coincide, as is required in the proof. It will be shown below that the isolated symmetries may be reduced to the site symmetries in a common coordinate system. Ror example 3, $G'(A) = G'(\underline{A}) = D_{\infty h}$, but in the common coordinate system $G''(A) = G''(\underline{A}) = C_{2v}$. In

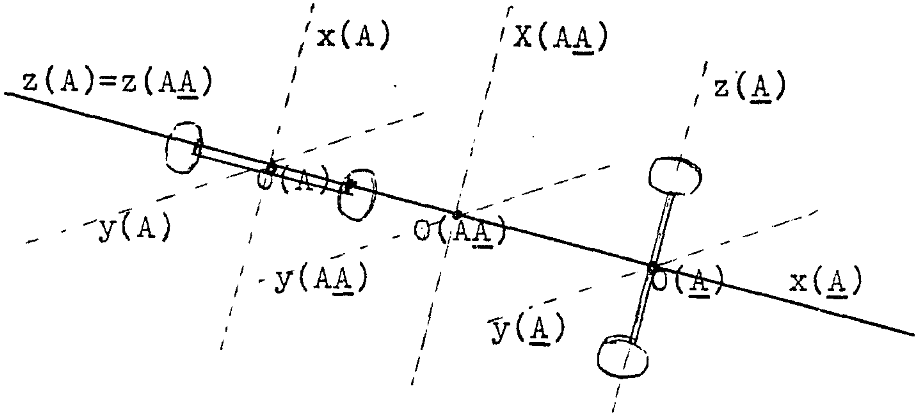
example 4, $G'(A) = C_{\infty v}$; $G'(\underline{A}) = D_{\infty h}$, while in the common coordinate system $G''(A) = C_{\infty v}$ and $G''(\underline{A}) = C_{2v}$. For these reduced groups, the invariant points do coincide and the theorem applies.

Common Coordinate System

The Theorem of Group Intersection may be extended to situations in which the invariant points of the two systems do not coincide by redefining the symmetry of each system in terms of a common coordinate system. System A has symmetry $G(A)$ with an implicit coordinate system $C(A)$, while $G(\underline{A})$ and $C(\underline{A})$ are similarly defined for system $\underline{A}$. Connect the origins of $C(A)$ and $C(\underline{A})$ to establish a composite coordinate system, $C(A\underline{A})$, with its origin at the center of mass of the composite system. The center of mass must be on the line connecting the origins since the center of mass of each system is at its individual origin. Treating the systems as point masses and connecting them allows us to treat the center of mass of the composite system by determining the point on the line which equalizes the two moment arms. This point is the center of mass of the composite system and the origin of the common coordinate system. Any other axis not symmetry determined (occurring in both systems) may be chosen arbitrarily.

As an example, consider the two systems, each with isolated symmetry $D_{\infty h}$. For the composite system to have symmetry $D_{\infty h} = D_{\infty h} \cap D_{\infty h}$, the intersection symmetry, the systems must have their coordinate systems superimposed: $C(A\underline{A}) = C(A) = C(\underline{A})$, or the intersection theorem as stated is not applicable. Defining $C(A\underline{A})$ allows us to treat arbitrary orientations.

Figure II - Common Coordinate System



Consider the situation when $z(A)$ is perpendicular to $z(\underline{A})$ at the origin of $C(\underline{A})$. The line connecting the origins establishes $z(A\underline{A})$ $(=z(A))$ and $y(A\underline{A})$ is chosen to be parallel to $z(\underline{A})$, determining the position of $x(A\underline{A})$. Now determine the symmetry of each system with respect to $C(A\underline{A})$ - $G''(A)$ and $G''(\underline{A})$.

(1) If the system has a C_n axis, it will be a symmetry element in G'' if and only if the C_n axis is colinear with $z(A\underline{A})$.

(2) A mirror plane in $G(A)$ or $G(\underline{A})$ will be retained if and only if it contains $z(A\underline{A})$.

(3) The resultant point group can contain no inversion point or other S_n axis unless $C(A\underline{A}) = C(A) = C(\underline{A})$. In this case the $C(A\underline{A})$ symmetry is clearly the full symmetry of the isolated system.

For the example shown above:

isolated symmetry	$G(A) = D_{\infty h}$	$G(\underline{A}) = D_{\infty h}$
$C(A\underline{A})$ symmetry elements	$E, C_{\infty v}, \infty\sigma_v$	$E, C_2(z), \sigma(xz)$ $\sigma(yz)$
$C(A\underline{A})$ symmetry group	$G''(A) = C_{\infty v}$	$G''(\underline{A}) = C_{2v}$

Since the isolated points of $G''(A)$ and $G''(\underline{A})$ coincide by construction, the Intersection Theorem now applies and, in the absence of Interchange operations:

$$G(A\underline{A}) = G''(A) \cap G''(\underline{A}) \qquad \text{(II.8)}$$

For the case under consideration:

$$G(A\underline{A}) = C_{\infty v} \cap C_{2v}$$

$$G(A\underline{A}) = C_{2v}$$

It will be seen later in the development of the Correlation Method[9] that the determination of $G''(A)$ and $G''(\underline{A})$ in the common coordinate system is equivalent to finding the site symmetry of A and $\underline{A}$ at the origin of $C(A\underline{A})$.

---

[9] See below, p. 26

Tensor Properties of crystals

The Theorem of Group Intersection is directly applicable to crystal properties relating an independent variable tensor and a dependent quantity tensor:[10]

$$\underset{\sim}{D} = \underset{\sim}{P}\ \underset{\sim}{I} \qquad \text{(II.9)}$$

It allows us to determine the symmetry of the property tensor and the dependent variable tensor and thus gives the form of those tensors by indicating the maximum number of independent variables allowed by symmetry.

The proof indicates that the symmetry governing the Hamiltonian of a composite system, $G(A\underline{A})$, equals the intersection group $G'(A) \cap G'(\underline{A})$ for a crystal and a field, since there are no interchange operations. A connection can be made between the composite symmetry and the symmetry of tensors of crystal properties. The dependent variable $\underset{\sim}{D}$ is a tensor representing a measureable property for a system consisting of a crystal in a field. Like any other observable, its expectation value can be represented for a particular state of the system in terms of an operator and the wave function of the state:[11]

$$\overline{D}(i) = \langle\, \psi(A\underline{A}i) / \hat{D} / \psi^{*}(A\underline{A}i) \,\rangle \qquad \text{(II.10)}$$

---

[10] J.A. McMillan, op. cit., p.793.
[11] P. Stehle, Quantum Mechanics, p.254.

or, for a statistical ensemble with weighting factors c_i:

$$\bar{D} = \sum_i c_i \langle \Psi(A\underline{A}i) \,/\, \hat{D} \,/\, \Psi^*(A\underline{A}i) \rangle \qquad (II.12)$$

For a non-degenerate state, $\Psi(A\underline{A}i)$ belongs to a one-dimensional representation of the group of the Hamiltonian, so that $\Psi_i \Psi_i^*$ spans the totally symmetric representation of $G(A\underline{A})$. If $\bar{D}(i)$ is to be non-zero, the symmetry group of $\hat{D}$ must also span the totally symmetric representation of $G(A\underline{A})$. Therefore $G(A\underline{A}) \subseteq G(\underset{\sim}{D})$ and $G(A\underline{A})$ determines the minimum symmetry of $G(\underset{\sim}{D})$; the intersection of crystal and field symmetry is included in the symmetry of the dependent variable.

The ranks of the independent variable and the dependent quantity tensors determine the rank of the property tensor:[12]

$$\mathrm{rank}(\underset{\sim}{P}) = \mathrm{rank}(\underset{\sim}{D}) + \mathrm{rank}(\underset{\sim}{I}) \qquad (II.13)$$

and the symmetry of the property tensor and of the independent variable tensor determine the minimum symmetry of the dependent quantity tensor, since any element common to both must be a symmetry element in their product:

$$G(\underset{\sim}{D}) = G(\underset{\sim}{P}) \cap G(\underset{\sim}{I}) \qquad (II.14)$$

The Intersection Theorem, as stated by McMillan,[13] predicts the symmetry, $G(\underset{\sim}{P})$, of the property tensor:

$$G(\underset{\sim}{P}) = G(\mathrm{crystal}) \cap G(\mathrm{field}) \qquad (II.15)$$

Some of the thermal, electrical and mechanical properties of crystals governed by this equation are

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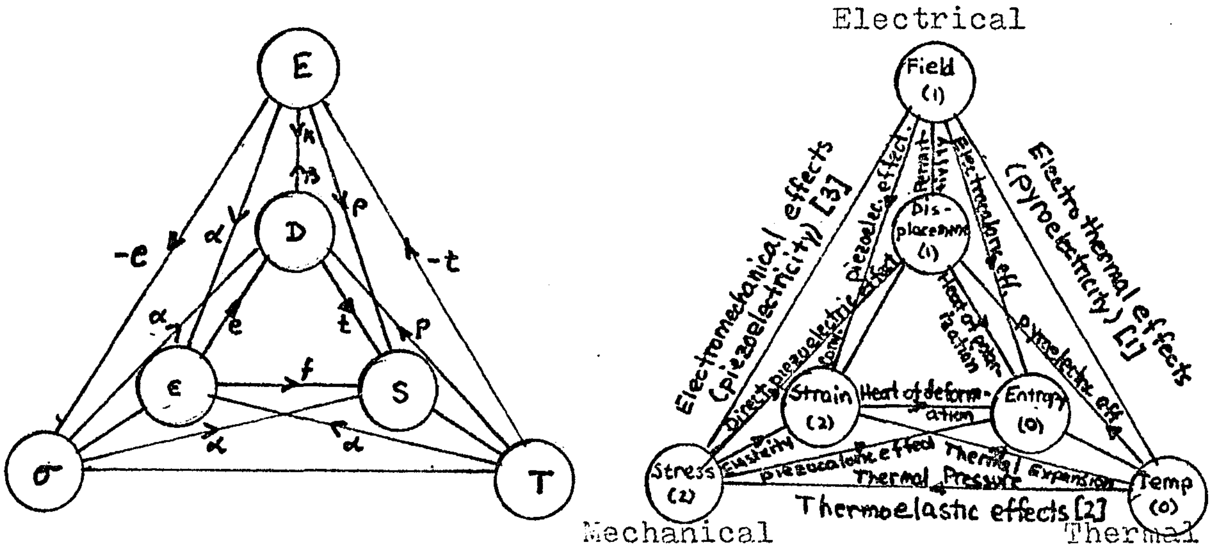
12. J.A. McMillan, op. cit., p.793.
13. J.A. McMillan, ibid.

Fig. IIA. Crystal Properties



The relationships between the thermal, electrical and mechanical properties of a crystal, showing the names of the properties and the variables, and the corresponding symbols. The tensor rank of the variables is shown in round brackets and the tensor rank of the properties in square brackets.[13a]

---

diagramatically expressed in figure IIA. Several of these properties will be discussed in more detail later.

(II.15) together with a knowledge of additional symmetry elements required mathematically for a particular property tensor, allows us to write the general form for the property tensor of a given symmetry

[13a] J.F. Nye, op. cit.

in a particular orientation in a field of known symmetry.

For all tensors of rank 1 (vectors) and polar tensors of rank 2, the information necessary is immediately accessible in the character tables.[14] To be non-zero, a component must transform as the totally symmetric representation of the Intersection Group. For polar vectors, we consider the representations of x, y, and z, and for axial vectors those of R_x, R_y, and R_z. An example for a polar vector is developed by McMillan[15]. The magnetic polarization, an axial vector, can be treated similarly by listing the point groups which are intersections of one of the thirty-two crystallographic point groups and the symmetry of the magnetic field, $C_{\infty h}$. The transformation of R_x, R_y, and R_z is then considered in each appropriate group to give the form of (P_x, P_y, P_z).

Figure III. Form of the magnetic property tensor

Point groups	R_x	R_y	R_z
C_1	P_x	P_y	P_z
C_s: (1st)	0	0	P_z
(2nd)	0	P_y	0
C_2, C_3, C_4, C_6 C_{2h}, C_{3h}, C_{6h}, S_4, S_6	0	0	P_z

For all point groups which are not subgroups of $C_{\infty h}$ no rotation, and thus no axial component, transforms as the totally symmetric representation.

---

[14] see Appendix B.

[15] J.A. McMillan, op. cit., p.794.

For rank 2 polar tensors corresponding results are obtained by considering the tensor in dyadic form:

$$T = \begin{matrix} T_{11}k_1k_1 & T_{12}k_1k_2 & T_{13}k_1k_3 \\ T_{21}k_2k_1 & T_{22}k_2k_2 & T_{23}k_2k_3 \\ T_{31}k_3k_1 & T_{32}k_3k_2 & T_{33}k_3k_3 \end{matrix} \qquad (II.16)$$

Where k_1 corresponds to x, k_2 to y, and k_3 to z.

For the rank 2 property tensors in electric polarization, the character tables are used by observing the transformation of pairs of unit vectors.

Figure IV. Form of the electric polarization property tensor.

Point group	xx	yy	zz	xy	xz	yz
C_1	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
C_s(1st)	T_{11}	T_{22}	T_{33}	T_{12}	0	0
(2nd)	T_{11}	T_{22}	T_{33}	0	T_{13}	0
C_2(1st)	T_{11}	T_{22}	T_{33}	T_{12}	0	0
(2nd)	T_{11}	T_{22}	T_{33}	0	T_{13}	0
C_{2v}	T_{11}	T_{22}	T_{33}	0	0	0
$C_3, C_4, C_6,$ C_{3v}, C_{4v}, C_{6v}	T_{11}	T_{11}	T_{33}	0	0	0

Most second-rank property tensors are symmetrical ($T_{ij} = T_{ji}$), so these coefficients define the tensor.

If we were considering a crystal in a second rank tensor field (O(3), $D_{\infty h}$, D_{2h}) other intersection groups would also be possible. Since all point groups are subgroups of O(3), the rest of the 32 crystal point groups could also occur as intersection symmetries.

Figure V. Form of second rank tensors.

Point group	xx	yy	zz	xy	xz	yz
C_i	T_{11}	T_{22}	T_{33}	T_{12}	T_{13}	T_{23}
C_{2h}(1st)	T_{11}	T_{22}	T_{33}	T_{12}	0	0
C_{2h}(2nd)	T_{11}	T_{22}	T_{33}	0	T_{13}	0
D_2,D_{2h}	T_{11}	T_{22}	T_{33}	0	0	0
C_{3h},C_{4h},C_{6h}, D_3,D_4,D_6,D_{2d}, D_{3h},D_{4h},D_{6h}, D_{3d},C_{3i},S_4	T_{11}	T_{11}	T_{33}	0	0	0
O_h,O,T_d,T_h,T	T	T	T	0	0	0

These results can also be obtained by taking the direct product of the representations of k_i and k_j, realizing that the product will contain the totally symmetric representation only if k_i and k_j belong to the same representation (the diagonals k_ik_j obviously always do). If the pair (x,y) spans an E representation (doubly degenerate), then xx+yy transforms as the totally symmetric representation and $T_{11} = T_{22}$. In the cubic groups, (x,y,z) spans a T (triply degenerate) representation, so thet xx+yy+zz spans the totally symmetric representation and T_{11}, T_{22} and T_{33} are the same by symmetry.

This second method employing direct products of unit vectors is more general and can be applied to the symmetry of a tensor of any rank whose unit vectors are either axial or polar. We can predict the symmetry of the tensor in a particular point group by determining for every combination of unit vectors whether the representation of $k_i k_j \ldots k_n$ is totally symmetric.

Double Groups

For both magnetic and electric polarization a consideration of the point groups alone of the crystal and field predicts the form of the property tensor and polarization vectors. For electric polarization, the point group determines whether there can be spontaneous polarization - in the absence of an imposed field the property tensor, and hence the Intersection Group, must contain the symmetry of the crystal (Neumann's Principle[16]) so that spontaneous polarization and the concommitant pyroelectricity can be observed only when the intersection symmetry is equal to the crystal symmetry. Magnetic polarization is stated by McMillan[17] to occur spontaneously in all thirty-two crystallographic point groups since it does not involve molecular rearrangement.

A more complete representation of the symmetry can be obtained by using double, or bi-color, groups. By introducing a time reversal operator, R_t, in a magnetic field, a new symmetry operator $R_t \cdot \sigma_v$ is defined, as detailed in McMillan's paper.[18] Similarly. $R_c \cdot i$,

[16] J.F. Nye, Physical Properties of Crystals, p.14.
[17] J.A. McMillan, op. cit., p.794.
[18] ibid.

determined by a charge conjugation operator, is a symmetry operation for an electric field. We can define the full symmetry bi-color groups:

$$G_M(G) = G + R_t \cdot \sigma_v \cdot G \qquad \text{(II.17)}$$

and
$$G_E(G) = G + R_c \cdot i \cdot G \qquad \text{(II.18)}$$

For the fields themselves we have:

Magnetic: $D_{\infty h}(C_{\infty h}) = C_{\infty h} + R_t \cdot \sigma_v \cdot C_{\infty h}$ (II.19)

Electric: $D_{\infty h}(C_{\infty v}) = C_{\infty v} + R_c \cdot i \cdot C_{\infty v}$ (II.20)

Similar double groups can be defined for each point group.

Figure VI. The full magnetic and electric groups for C_{2v} and C_{2h} crystal point group symmetry, and their intersections with the full magnetic and electric field symmetry.

C_{2v}	E	$C_2(z)$	$\sigma(xz)$	$\sigma(yz)$
$R_t\sigma(xz) \cdot C_{2v}$	$R_t\sigma(xz)$	$R_t\sigma(yz)$	R_t	$R_tC_2(z)$
	$\underline{C_{2v}(C_{2v}) = C_{2v} + R_t\sigma(xz) \cdot C_{2v}}$			
$R_c i \cdot C_{2v}$	$R_c i$	$R_c\sigma(xy)$	$R_cC_2(y)$	$R_cC_2(x)$
	$\underline{D_{2h}(C_{2v}) = C_{2v} + R_c i \cdot C_{2v}}$			

C_{2h}	E	$C_2(z)$	i	$o(xy)$
$R_t\sigma(xz) \cdot C_{2h}$	$R_t\sigma(xz)$	$R_t\sigma(yz)$	$R_tC_2(y)$	$R_tC_2(x)$
	$D_{2h}(C_{2h}) = C_{2h} + R_t\sigma(xz) \cdot C_{2h}$			
$R_c i \cdot C_{2h}$	$R_c i$	$R_c\sigma(xy)$	R_c	$R_cC_2(z)$
	$\underline{C_{2h}(C_{2h}) = C_{2h} + R_c i \cdot C_{2h}}$			

Magnetic Field Intersection

	$D_{\infty h}(C_{\infty h})$
$C_{2v}(C_{2v})$	$C_{2v}(C_2)$
$D_{2h}(C_{2h})$	$D_{2h}(C_{2h})$

Electric Field Intersection

	$D_{\infty h}(C_{\infty v})$
$D_{2h}(C_{2v})$	$D_{2h}(C_{2v})$
$C_{2h}(C_{2h})$	$C_{2h}(C_2)$

In both the electric and magnetic groups the tensor symmetry is given by the point group portion of the intersection symmetry. C_{2v} crystals will show spontaneous polarization while C_{2h} crystals will not, since a descent of symmetry to C_2 would be required by the Intersection Theorem in the latter case. Both C_{2v} and C_{2h} crystals may exhibit magnetic polarization since the crystal itself does not have to distort to lower the symmetry (in the case of a C_{2v} crystal, to C_2), since it can be lowered by spin alignment. The Intersection Theorem, then, predicts the total symmetry of the coupled system, but does not predict in what way the system must distort, or whether it can distort, to attain this symmetry. For those cases where molecular rearrangement would be required, the Intersection Theorem imposes a condition for spontaneity.

Applications

1. Pyroelectricity[19] $\Delta P_i = p_i \Delta T$ (II.21)

Here we have a first rank tensor relating a scalar and a vector for a crystal of symmetry G_c with a spontaneous electric field of symmetry $C_{\infty v}$. The Intersection Theorem predicts the symmetry of p_i to be at least $G(\text{crystal}) \cap C_{\infty v}$ and the spontaneity condition requires that $G(p_i)$ contain the full symmetry of the crystal, so that G(crystal) is limited to those crystal point groups which are subOgroups of $C_{\infty v}$. From McMillan's paper these are[20]:

Figure VII. Point groups exhibiting pyroelectricity, and the form of the polar vectors

Point group	x	y	z
C_1	P_x	P_y	P_z
C_s(1st)	P_x	P_y	P_z
(2nd)	P_x	0	P_z
C_2(1st)	0	0	P_z
(2nd)	0	P_y	0
$C_3, C_4, C_6,$ $C_{2v}, C_{3v}, C_{4v},$ and C_{6v}	0	0	P_z

To show pyroelectricity, a crystal must correspond to one of these ten point groups, and both p_i and P_i would have the form predicted above.

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[19] J.F. Nye, op. cit.

[20] J.A.McMillan, Op. cit., p.794.

From equation (II.14):

$$G(D) = G(P) \cap G(I)$$

$$G(P_i) = G(p_i) \cap G(T)$$

$$G(P_i) \supseteq (G(\text{crystal}) \cap G(\text{field})) \cap O(3)$$

$$G(P_i) \supseteq G(\text{crystal}) \cap C_{\infty v}$$

2. Direct Piezoelectric Effect[21]

$$P_i = d_{ijk}\sigma_{jk} \qquad \text{(II.22)}$$

($d_{ijk} = d_{ikj}$ since, in the absence of body torques, $\sigma_{jk} = \sigma_{kj}$.)

If a stress is applied to certain crystals they develop an electric moment whose magnitude is proportional to the applied stress. When a general stress σ_{jk} acts on a piezoelectric crystal, the polarization P_i is linearly related to all the components of σ_{jk}. The d_{ijk} are the piezoelectric moduli.

Since the stress tensor σ_{jk} is symmetric, it is diagonalizable:

$$o_{jk} = \begin{pmatrix} \sigma_{11} & 0 & 0 \\ 0 & \sigma_{22} & 0 \\ 0 & 0 & \sigma_{33} \end{pmatrix} \qquad \text{(II.23)}$$

The expression above gives the most general form of the stress tensor; even though it is of second rank, it is defined by at most three variables.

Figure VIII. Stress Symmetries.

1. uniaxial stress - $D_{\infty h}$

$$\begin{pmatrix} \sigma & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

2. biaxial stress - D_{2h}

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

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[21] J.F. Nye, op. cit. p.110.

3. triaxial stress - D_{2h}

$$\begin{pmatrix} \sigma_1 & 0 & 0 \\ 0 & \sigma_2 & 0 \\ 0 & 0 & \sigma_3 \end{pmatrix}$$

4. Hydrostatic pressure - O(3)

$$\begin{pmatrix} -p & 0 & 0 \\ 0 & -p & 0 \\ 0 & 0 & -p \end{pmatrix}$$

5. pure sheer stress - D_{2h}

$$\begin{pmatrix} -\sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

The stress tensor, in common with the strain tensor, can have any orientation within a crystal, and it can exist just as well in isotropic bodies like glass as in anisotropic crystals. In this respect it is like an imposed electric field, which can, of course, have an arbitrary direction in a crystal. Such tensors are called field tensors.

A property tensor of rank three has twenty-seven terms, but symmetry arguments reduce this to eighteen ($d_{ijk} = d_{ikj}$). An additional constraint, beyond that imposed by the Intersection Theorem, is that a third-rank tensor cannot be written for a point group that includes inversion, since the character under the i operation is -1, so the representation cannot transform as the totally symmetric representation. This is also true of a first-rank tensor, or of any tensor of odd rank. This problem did not arise in considering the symmetries allowed to first rank tensors, since only symmetries corresponding to sub-groups of $C_{\infty v}$ were given, which could not, therefore, contain i.

This gives us another selection rule for spontaneous phenomena. The maximum symmetry for a polar vector is $C_{\infty v}$, whether the vector is describing a crystal in a $C_{\infty v}$ field or not. Correspondingly, a property tensor of rank three cannot have a center of symmetry, since in centrosymmetric groups no third order term transforms as the totally symmetric representation. Thus a centrosymmetric crystal in a centrosymmetric rank two tensor field will have an identically zero rank three property tensor, and any physical property described by such a property tensor would not occur spontaneously.

For the non-centrosymmetric crystallographic point groups the non-zero components of the property tensor can be obtained from the character tables as follows.

1. $x=1$ $y=2$ $z=3$
2. In d_{ijk} the first subscript, i, corresponds to the single terms in the character tables, while jk corresponds to the second-order terms.
3. Take the product of first-order terms with second-order terms only when they correspond to the same representation, so that their product will correspond to the totally symmetric representation.
4. A product of terms corresponding to a degenerate representation has third order terms spanning

the totally symmetric representation as indicated in the following examples.

Figure IX. Products of terms spanning degenerate representations and resulting relationships between terms in third rank tensors.

E (x,y) · (yz,xz)

A (x·yz,- y·xz),(y·yz + x·xz)

$d_{123} = -d_{213} \quad d_{223} = d_{113}$

E (x,y) · (xx-yy,xy)

A (x·xx - x·yy - 2y·xy),(y·xx - y·yy + 2x·xy)

$d_{111} = -d_{122} = -2d_{112}; \; d_{211} = -d_{222} = 2d_{112}$

Products involving non-degenerate representations give only information about whether the value of d_{ijk} is zero or non-zero, while products involving degenerate representations give information about relationships between different components of d_{ijk}.

III. The Correlation Method

The Correlation Method used by Fateley[22] and others[23-26] to determine molecular and lattice vibrations and infrared and Raman selection rules, applies the principles of the correlation theorem in group theory according to the rules provided by Halford and Hornig.[27,28] Using benzene as an example, a step-by-step process is followed to determine the number, symmetry, and spectral activity of the normal vibrations of the molecule.[29]

1. The molecular symmetry must be known or determined.
2. The site symmetry for all equivalent sets of atoms (a set of atoms that can be transferred into one another by the symmetry operations present in the molecule) must be known or determined. The elements of symmetry of the molecular point group contained in or passing through the atom in question form a complete set of operations belonging to a specific point group - the site symmetry - which is clearly a subgroup of the molecular

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[22] W.G. Fateley, et. al., Infrared and Raman Selection Rules for Molecules and Lattice Vibrations, p.120.
[23] E. Rytter, Chem. Phys. 54, p.3293 (1976)
[24] J. Choisnet, J. Sol. St. Chem. 26, p.83 (1978)
[25] W.G. Harter, Rev. M. Phys. 50, p.37 (1978)
[26] J.C. Decius, J. Chem. Phys. 68, p.1715 (1978)
[27] D.F. Hornig, J. Chem. Phys. 16, p.1063 (1948)
[28] R.S. Halford, J. Chem. Phys. 17, p.607 (1949)
[29] W.G. Fateley, op. cit.

point group.

3. The symmetry representation of the translation vectors is determined for each site group from the character tables. The transformation of these representations in the point group of the molecule is determined from the correlation tables.[30] Only one representative atom of each equivalent set need be considered. The number of atoms in the set (Z) is inherent in the site symmetry: to have C_{2v} site symmetry in a molecule of D_{6h} symmetry, an atom must occupy one of six equivalent sites. A single translation vector in C_{2v} will then correlate to a set of representations in D_{6h} whose dimensions add up to six, insuring the appropriate total number of molecular motions in the system.

4. The irreducible representations for the molecule (Γ^{mol}) obtained include both the genuine normal vibrations ($\Gamma^{\mathrm{mol\ vib}}$) and the pure rotations and translations of the molecule. These non-genuine motions can easily be removed by subtraction of the representations for rotations (R_x, R_y, R_z) and translations (T_x, T_y, T_z) obtained from the character tables for the overall molecular symmetry.

$$\Gamma^{\mathrm{mol\ vib}} = \Gamma^{\mathrm{mol}} - \Gamma^{\mathrm{trans}} - \Gamma^{\mathrm{rot}} \qquad \text{(III.1)}$$

5. Identification of the spectral activity of each species of the molecular point group.

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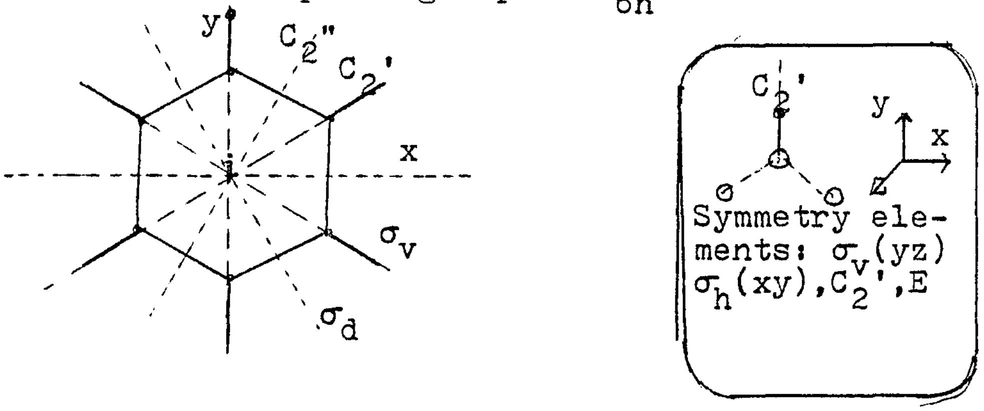
[30] See Appendix C

Benzene Symmetry

1. The z axis is perpendicular to the molecule's plane (σ_h) and passes through the inversion point (i) found in the center of the hexagon. The z axis contains the elements of symmetry C_6, C_3, C_2, S_6, and S_3 not shown in the figure below.

Figure X. Molecular and site symmetries of benzene. The molecular point group is D_{6h}.[31]



2. The isolated portion at the right of figure X considers only one hydrogen atom. It illustrates the presence of only those symmetry elements E, C_2', $\sigma_v(yz)$, and $\sigma_v(xy)$. Thus, the site symmetry of the hydrogen is C_{2v}. The carbon atoms are similarly situated, with the same elements of symmetry passing through them, so the site symmetry of the carbon atoms is the same (C_{2v}).

3. From the C_{2v} character tables, T_z transforms as the totally symmetric representation (A_1), T_x transforms as B_1, and T_y as B_2. Correlating the representations in C_{2v} to D_{6h} (the C_2' axis is retained in C_{2v}):

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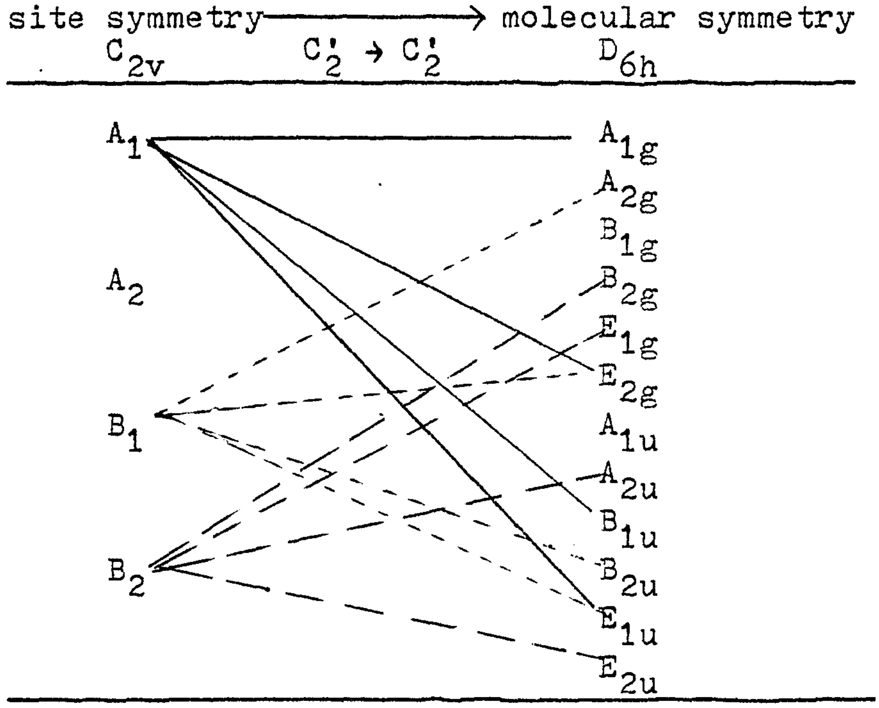
[31] W.G. Fateley, op. cit. p.67.

$$\Gamma^{H} = A_{1g} + A_{2g} + B_{2g} + E_{1g} + 2E_{2g} + A_{2u} + B_{1u} + 2E_{1u} + E_{2u} \qquad \text{(III.2)}$$

Figure XI. The correlation between site and molecular symmetry species for the hydrogen atom in benzene.[32]



4. The site symmetry and Z value (= 6) of carbon are exactly the same as hydrogen; therefore, $\Gamma^{H} = \Gamma^{C}$.

$$\Gamma^{mol} = \Gamma^{H} + \Gamma^{C}$$

$$\Gamma^{mol\ vib} = \Gamma^{mol} - \Gamma^{rot} - \Gamma^{trans}$$

$$\Gamma^{rot} = A_{2g} + E_{1g}$$

$$\Gamma^{trans} = A_{2u} + E_{1u}$$

$$\Gamma^{mol\ vib} = 2A_{1g}(R) + A_{2g}(0) + 2B_{2g}(0) + E_{1g}(R) + 4E_{2g}(R) + A_{2u}(IR) + 2B_{1u}(IR) + 2B_{2u}(0) + 3E_{1u}(IR) + 2E_{2u}(0) \qquad \text{(III.3)}$$

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32. W.G. Fateley, op. cit. p. 68.

5. (IR) indicates infra-red activity, (R) is Raman active and (O) shows no spectral activity. This method predicts four infra-red fundamentals, seven Raman fundamentals, and no coincidences, as would be predicted for a centrosymmetric molecule.

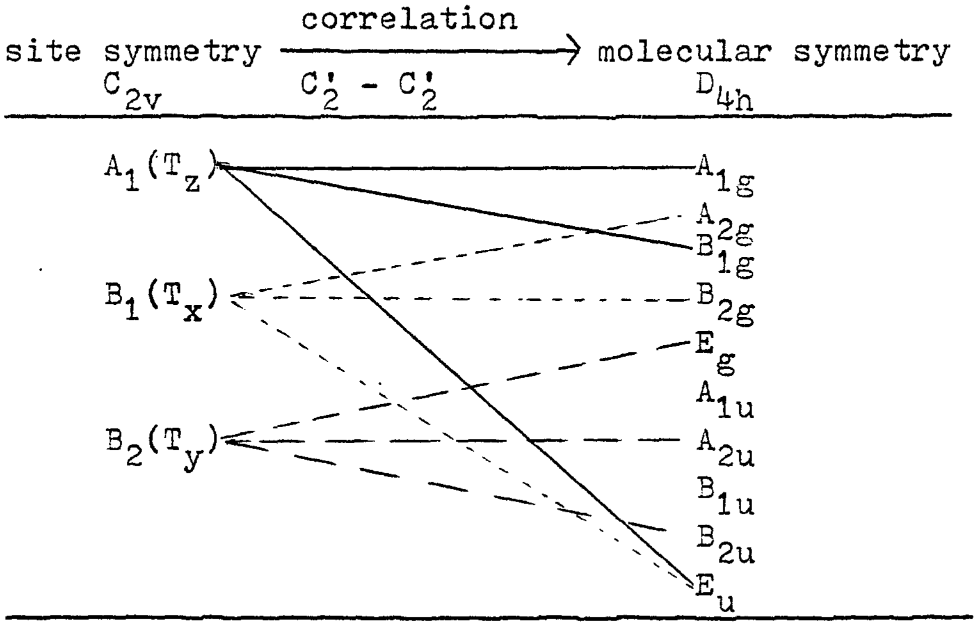
Applications involving normal mode vibrations

1. Ring distortions of cyclobutadiene

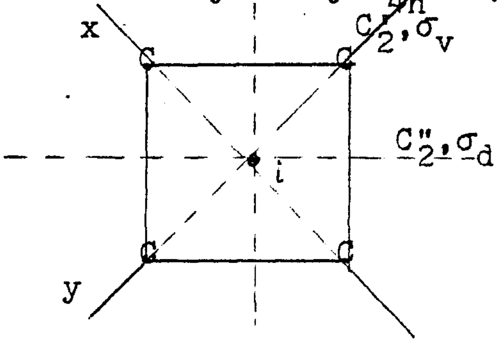
The correlation method is used to determine a set of distortions for a hypothetical square-planar cyclocutadiene ring. These are not necessarily vibrations of the ring, since the geometry considered is not necessarily a minimum in the potential curve for all possible distortions. Since any possible distortion of the molecule from a given base geometry can be expressed in terms of a weighted sum of the normal modes, the set forms a useful coordinate system for discussing possible stable geometries of the molecule.

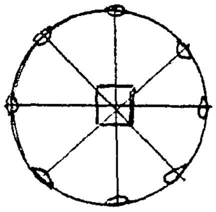
For cyclobutadiene, the correlation method is applied in finding the normal modes of the square-planar geometry, and the symmetries of the six ring vibrations are considered as alternate geometries. The vibrations of the distorted cyclobutadienes can be determined directly from the correlation table for D_{4h}, rather than by repeating the correlation method determination for each distorted geometry.

Figure XII. The correlation between site and molecular symmetry for the carbon atoms of CBD (Z =4)

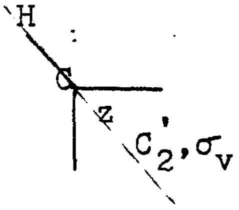


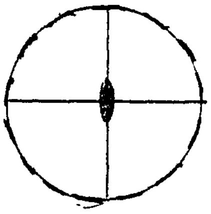
Molecular symmetry D_{4h}: $E, 2C_4, C_2, 2C_2', 2C_2'', i, 2S_4, 2\sigma_v, 2\sigma_d$





Site symmetry $C_{2v}(C_2')$: $E, C_2, \sigma_v(xz), \sigma_v(yz)$





$$\Gamma^C = A_{1g}+A_{2g}+B_{1g}+B_{2g}+E_g+A_{2u}+B_{2u}+E_u \qquad \text{(III.4)}$$

Corrected for rotations and translations, these will give the distortions of the ring. If we wish the vibrations of a square-planar C_4H_4 molecule, we must also include the hydrogen atoms. Since the site symmetry is the same, $\Gamma^{H} = \Gamma^{C}$, and

$$\Gamma^{mol} = 2A_{1g}+2A_{2g}+ 2B_{1g}+2B_{2g}+2A_{u}+2B_{2u}+4E_{u}$$

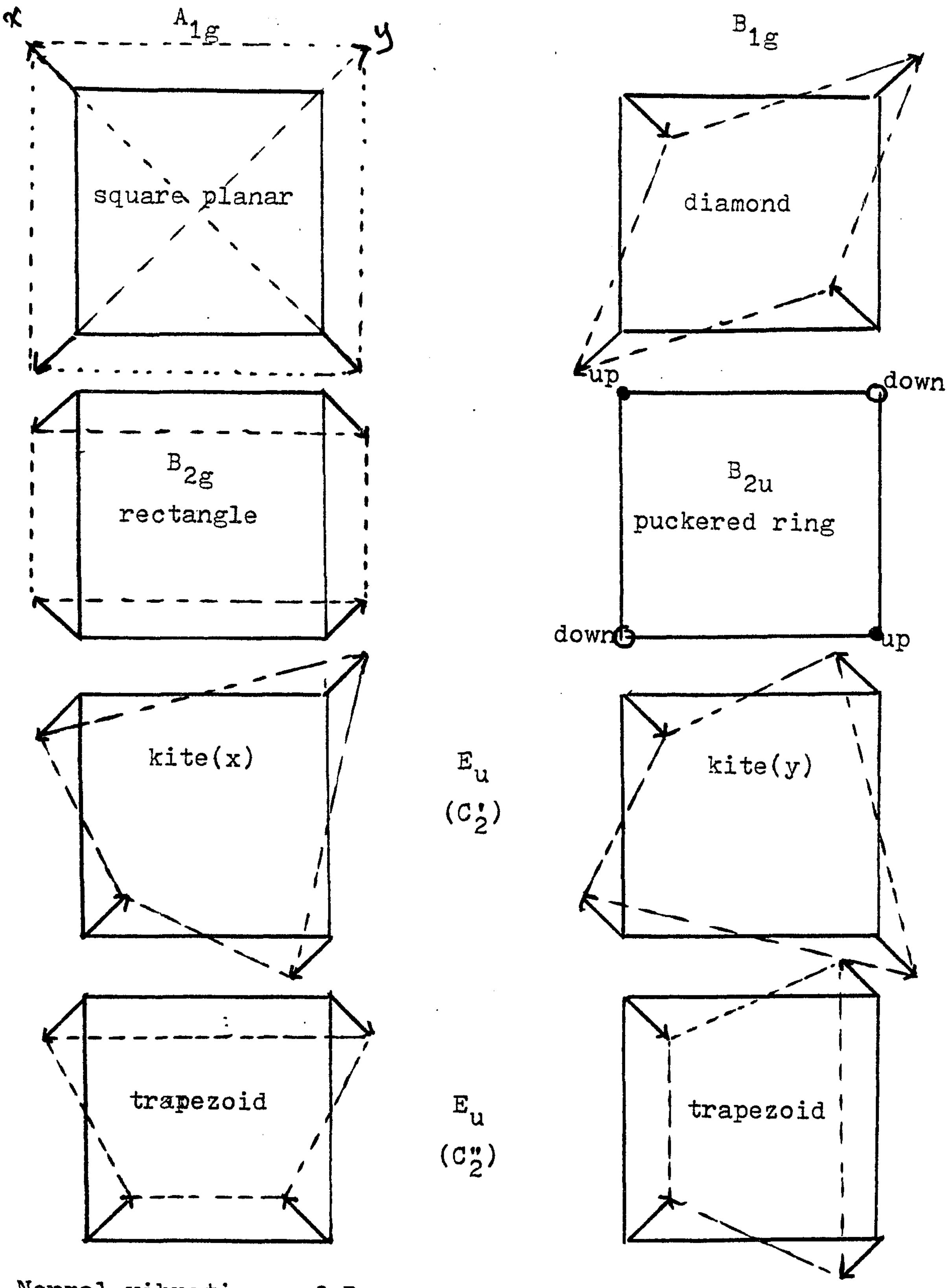
$$\Gamma^{rot} = A_{2g}+E_{g}$$

$$\Gamma^{trans} = A_{2u}+E_{u}$$

$$\Gamma^{mol\ vib} = 2A_{1g}(R) + A_{2g}(0) + 2B_{1g}(R) + 2B_{2g}(R) + E_{g}(R) + A_{2u}(IR) + 2B_{2u}(0) + 3E_{u}(IR)$$

$$\text{Ring distortions: } A_{1g} + B_{1g} + B_{2g} + B_{2u} + E_{u} \quad \text{(III.5)}$$

Each ring distortion gives rise to a distorted geometry. To find the appropriate geometry, consider the highest symmetry in the correlation table for D_{4h} in which the totally symmetric representation corresponds to the irreducible representation of the distortion. Thus, the distortion of A_{1g} symmetry belongs to the D_{4h} point group itself, while the B_{1g} distortion corresponds to a representation of $D_{2h}(C_2')$, the symmetry of a diamond (rhombus), which is the distortion of a square that retains the C_2' axes (those containing the atoms). For one-dimensional representations, this symmetry information can also be obtained from the character tables by noting those operations in the D_{4h} character table that are equal to 1 in the B_{1g} representation, or the representation of interest. The group formed by these operations is the symmetry point group of the distorted ring, and this method is clearly equivalent to the former. For the other one-dimensional representations both methods agree in assigning symmetry point groups to the distortions, but for the two-dimensional representation the character tables list only the trace of the representation, restricting us to the first method. Since E_u



Normal vibrations of D_{4h}

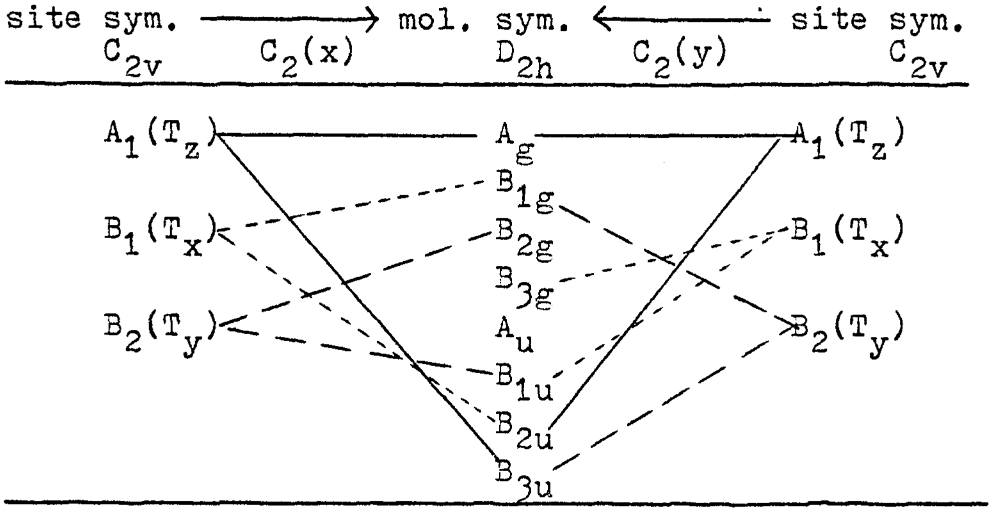
Figure XIII.

correlates to A_1+B_1 in C_{2v} with either the C_2' or the C_2'' axis retained in the distortion, there appear at first to be two sets of degenerate E_u distortions. With the C_2' axis retained, a set of degenerate kite-shaped distortions is formed, with either x or y in D_{4h} becoming the major axis in C_{2v}. If y is chosen as the new z axis, the kite shape with y as its major axis corresponds to the A_1 representation in C_{2v}, while the kite symmetric about the former x axis corresponds to B_1. Choosing to retain the two C_2'' axes results in two trapezoids, again corresponding to A_1 and B_1 in C_{2v}. However, if the sum of the two degenerate kite-shaped distortions is taken geometrically, it results in the trapezoidal symmetry with one of the C_2'' axes retained, while the difference of the kites gives the other trapezoid. Similarly, the sum and difference of the two trapezoidal distortions yields the kites, showing that only one independent E_u distortion exists for the ring.

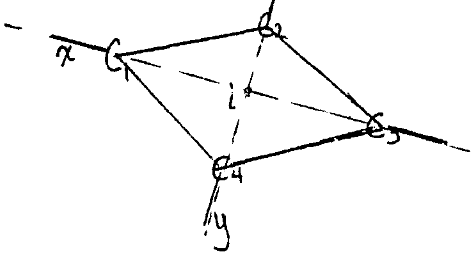
The normal modes and their predicted spectral activity can be found for each of the distortions by applying the correlation method as before, or simply by correlation of the vibrations in D_{4h} into the lower symmetry and finding the spectral activity from the character tables. Both approaches are illustrated for the diamond-shaped distortion resulting from the B_{1g} normal mode of square-planar cyclobutadiene (CBD), and the results for the other distorted rings are obtained by the second method.

The B_{1g} distortion of the ring gives rise to D_{2h} symmetry with both C_2' axes retained, along with the C_2 operation colinear with the z axis, so the axis identification remains the same as in the original square. Carbon atoms 1 and 3 occupy equivalent sites of site symmetry C_{2v} with the x axis retained as C_2. Carbons 2 and 4 are also on equivalent sites with site symmetry $C_{2v}(C_2(y))$.

Figure XIV. The correlation between site and molecular symmetry for the carbon atoms of rhomboid CBD



$$\Gamma^{C} = \Gamma^{H} = 2A_g + 2B_{1g} + B_{2g} + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$$
$$\Gamma^{mol} = \Gamma^{C} + \Gamma^{H} = 4A_g + 4B_{1g} + 2B_{2g} + 2B_{3g} + 4B_{1u} + 4B_{2u} + 4B_{3u}$$
$$\Gamma^{rot} = B_{1g} + B_{2g} + B_{3g}$$
$$\Gamma^{trans} = B_{1u} + B_{2u} + B_{3u}$$
$$\Gamma^{mol\ vib} = 4A_g + 3B_{1g} + B_{2g} + B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u} \qquad \text{(III.6)}$$



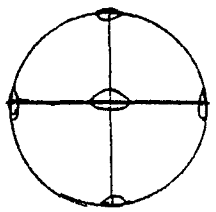
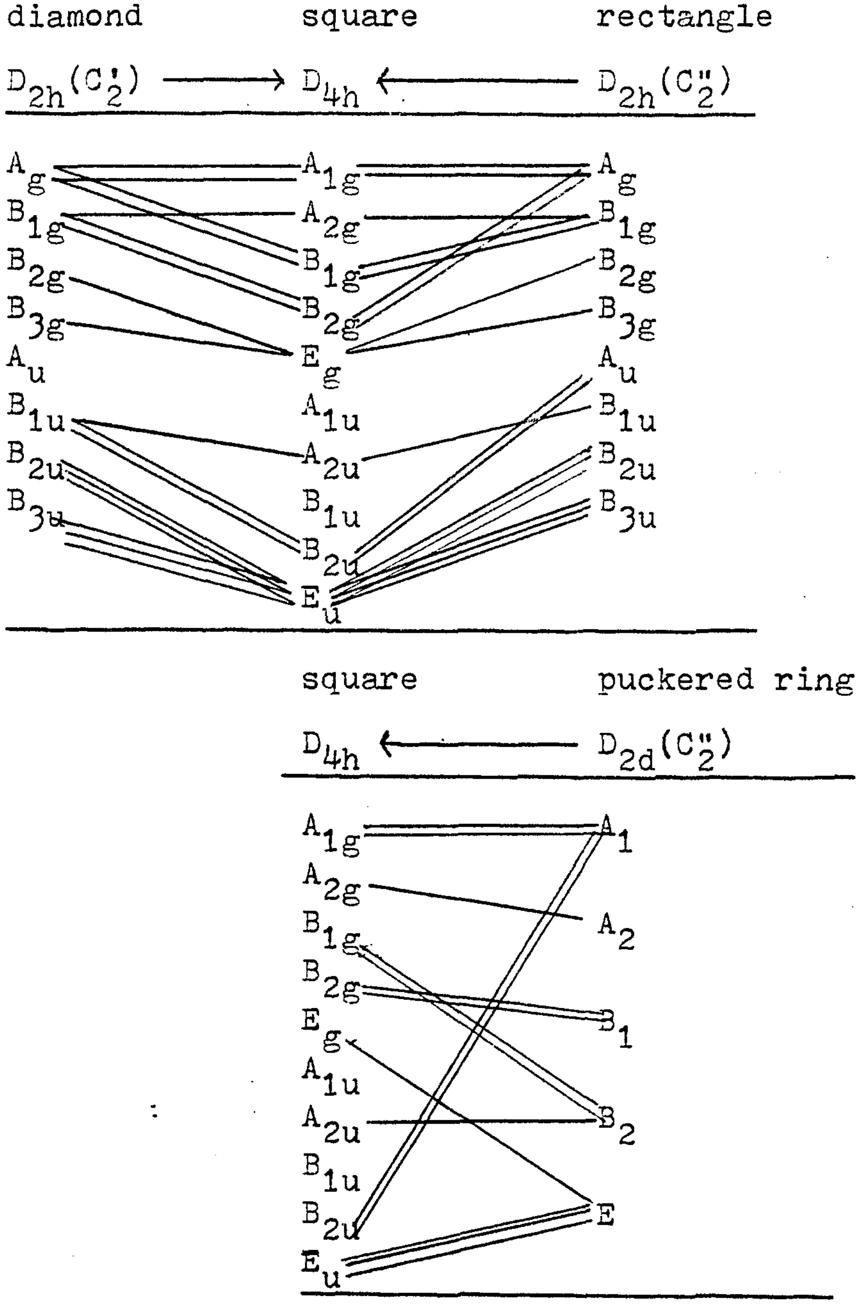


Figure XV. Correlations between D_{4h} and ring distortion geometries.



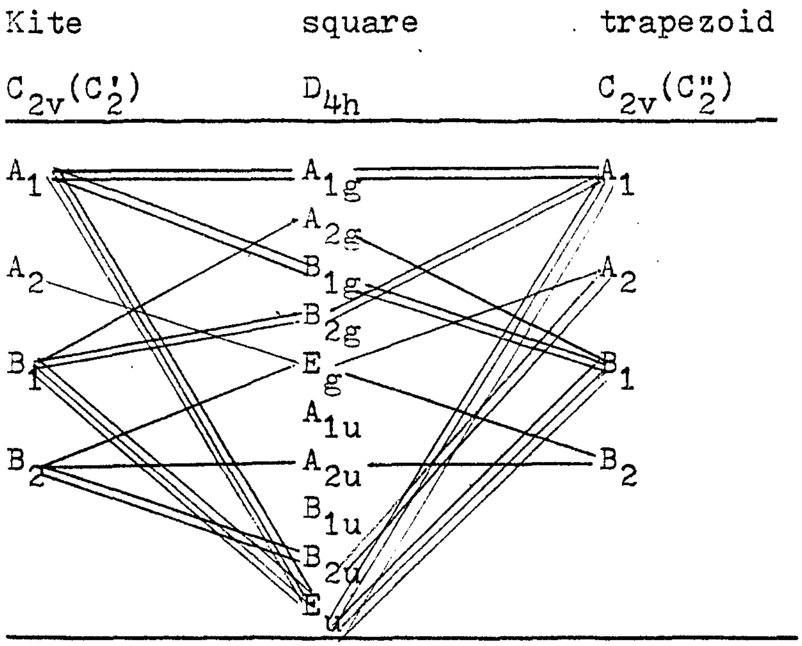


Figure XVI. Molecular vibrations in distorted geometries

$$\Gamma^{\text{mol vib}}_{D_{2h}(C_2')} = 4A_g(R)+3B_{1g}(R)+B_{2g}(R)+B_{3g}(R)+3B_{1u}(IR)+3B_{2u}(IR)+3B_{3u}(IR)$$

$$\Gamma^{\text{mol vib}}_{D_{2h}(C_2'')} = 4A_g(R)+3B_{1g}(R)+B_{2g}(R)+B_{3g}(R)+2A_u(0)+B_{1u}(IR)+3B_{2u}(IR)+3B_{3u}(IR)$$

$$\Gamma^{\text{mol vib}}_{D_{2d}(C_2'')} = 4A_1(R)+A_2(0)+2B_1(R)+3B_2(IR,R)+4E(IR,R)$$

$$\Gamma^{\text{mol vib}}_{C_{2v}(C_2')} = 7A_1(IR,R)+A_2(R)+6B_1(IR,R)+4B_2(IR,R)$$

$$\Gamma^{\text{mol vib}}_{C_{2v}(C_2'')} = 7A_1(IR,R)+3A_2(R)+6B_1(IR,R)+2B_2(IR,R)$$

		IR active	Raman active
D_{4h}	square planar	4	7
$D_{2h}(C_2')$	diamond	9	9
$D_{2h}(C_2'')$	rectangle	7	9
$D_{2d}(C_2'')$	puckered ring	7	13
$C_{2v}(C_2')$	kite	17	18
$C_{2v}(C_2'')$	trapezoid	15	18

Molecule in a Ligand Field

The Intersection Theorem does not apply only to crystal properties represented as tensors, but also to any composite system, such as an ion in a crystal field. While the Intersection Theorem applies to any ion in a crystal, it gives us no additional information about the problem when the symmetry of the free ion is O(3), since the intersection symmetry is merely the crystal field symmetry. For an ion which is not monoatomic, the Intersection Theorem is useful in determining the appropriate symmetry.

Consider an ion of symmetry G(I) in a crystal field of symmetry G(CF). For example, take the ammonium ion (T_d) in a square planar crystal(D_{4h}). If the major axes are parallel:

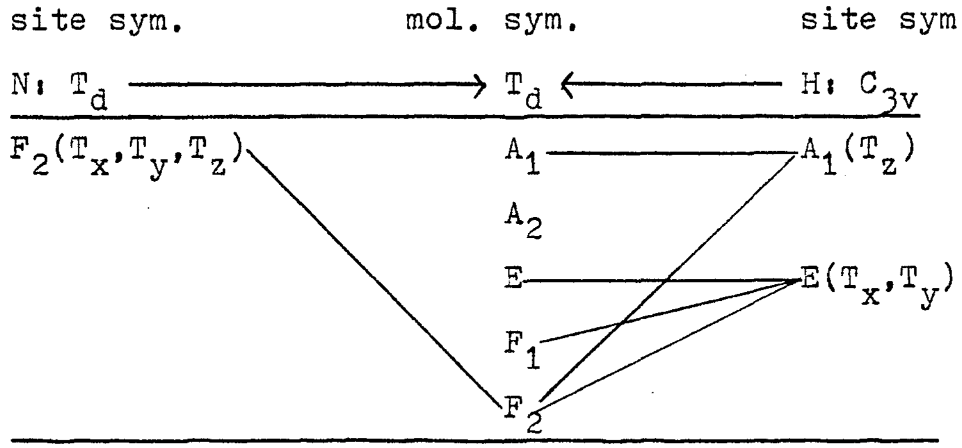
$$G = G(I) \cap G(CF) \qquad \text{(III.7)}$$

$$D_{2d} = T_d \cap D_{4h} \qquad \text{(III.8)}$$

We would then expect that the vibrations of the NH_4^+ ion would be governed by D_{2d} rather than T_d.

The Correlation Method is used to determine the vibrations of the isolated ammonium ion. The vibrations in all possible intersection symmetries (subgroups of T_d) are then obtained from the correlation tables, along with the symmetries of crystal fields of higher symmetry that would give rise to those intersections. Clearly, the crystal field must have at least the intersection symmetry.

Figure XVII. Correlation Method applied to NH_4^+



mol vib	for subgroups of T_d	IR	R
T_d	$A_1(R)+E(R)+2F_2(IR,R)$	2	4
T	$A(R)+E(R)+2F(IR,R)$	2	4
D_{2d}	$2A_1(R)+B_1(R)+2B_2(IR,R)+2E(IR,R)$	4	7
C_{3v}	$3A(IR,R)+3E(IR,R)$	6	6
S_4	$2A(R)+3B(R)+2E(IR,R)$	2	7
D_2	$3A(R)+2B_1(IR,R)+2B_2(IR,R)+2B_3(IR,R)$	6	9
C_{2v}	$4A_1(IR,R)+A_2(R)+2B_1(IR,R)+2B_2(IR,R)$	8	9
C_3	$3A(IR,R)+3E(IR,R)$	6	6
C_2	$5A(IR,R)+4B(IR,R)$	9	9
C_s	$6A'(IR,R)+3A''(IR,R)$	9	9

$T_d \quad T_h = T$

$T_d \quad D_{4h} = D_{2d} \; (S_4 = C_4)$

$T_d \quad D_{3h} = C_{3v} \; (C_3 = C_3)$

$T_d \quad D_{2h} = C_{2v} \; (S_4 = C_2)$

$T_d \quad C_{3h} = C_3 \; (C_3 = C_3)$

$T_d \quad C_{2h} = C_2 \; (S_4 = C_2)$

Molecular orbitals

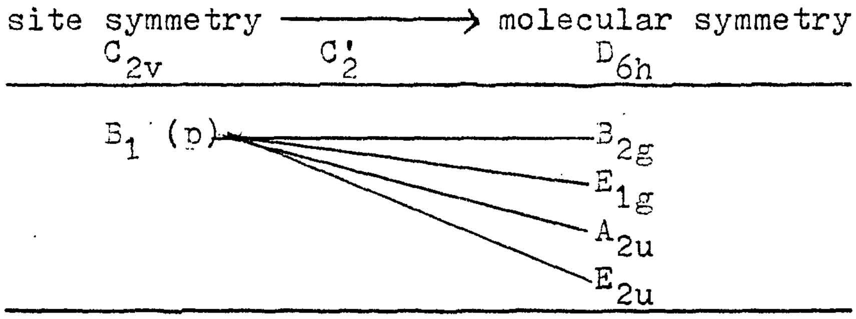
The form of the Correlation Method lends itself to determination of the symmetry of molecular orbitals composed of linear combinations of atomic orbitals. An atomic orbital or set of atomic orbitals is chosen on each atom, the site symmetries of the atoms are determined, and the representation of each orbital in the site symmetry is correlated with the molecular symmetry for each equivalent site.

As an example, the σ and pi-bonding orbitals are determined for benzene.

Pi-bonding in benzene

1. A p orbital perpendicular to the ring is chosen on each carbon.
2. All six carbons are equivalent and occupy $C_{2v}(C_2')$ sites.
3. The p orbital perpendicular to the ring is of B_1 symmetry in C_{2v}, since the x-axis is perpendicular to the plane of the molecule in C_{2v}.

Figure XVIII. Correlation Method applied to pi-bonding in benzene.



$$B_{2g}\text{:}\ p_1 - p_2 + p_3 - p_4 + p_5 - p_6$$

$$E_{1g}\text{:}\begin{cases} 2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6 \\ p_1 + 2p_2 + p_3 - p_4 - 2p_5 - p_6 \end{cases}$$

$$A_{2u}\text{:}\ p_1 + p_2 + p_3 + p_4 + p_5 + p_6$$

$$E_{2u}\text{:}\begin{cases} 2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6 \\ -p_1 + 2p_2 - p_3 - p_4 + 2p_5 - p_6 \end{cases}$$

The LCAO-MO's are determined by applying the operations of the group D_{6h} to a representative orbital and multiplying the result of each operation by its character in the appropriate representation. The process is self-correcting, since any representation not corresponding to an orbital gives a result of zero. A less time-consuming method for one-dimensional representations is to find in the correlation table for the group of the molecule (D_{6h}) the highest symmetry in which the orbital representation correlates with the totally symmetric representation. The appropriate orbital can then be written by inspection. For example, B_{2g} correlates with A_{1g} in $D_{3d}(C_2'')$. By symmetry, then, $p_1=p_3=p_5=-p_2=-p_4=-p_6$. The general form of multidimensional representations can be determined in the same manner, but coefficients of non-equivalent positions must be found in the character tables.

Sigma-bonding in benzene

1. The orbitals appropriate for sigma bonding are $1s_H$ (hydrogen), $1s_C$, $2s_C$ and two 2p orbitals in the plane of the molecule for the carbon atoms.

2. The six carbon atoms form an equivalent set of $C_{2v}(C_2')$ site symmetry, as do the six hydrogen atoms.

3. All s orbitals have A_1 symmetry in C_{2v}. For the sake of convenience, a set of symmetry related p orbitals is chosen rather than using the x and y directions of the benzene molecule. For each carbon there is one p orbital along the C_2' axis (positive direction outward) and another perpendicular to the C_2' axis, with the positive lobe in a clockwise direction from the carbon atom. The axial p orbital is then of A_1 symmetry in the C_{2v} site symmetry, since it lies along the major axis, and the perpendicular p orbital in the plane of the molecule is of B_2 symmetry in C_{2v}.

Figure XIX. Results of correlation for sigma bonding in benzene.

site sym. ⟶ Molecular symmetry

C_{2v} C_2' D_{6h}

$$4A_1 \longrightarrow 4A_{1g}+4E_{2g}+4B_{1u}+4E_{1u}$$

$$B_2 \longrightarrow A_{2g}+E_{2g}+B_{2u}+E_{1u}$$

Since the four A_1 orbitals behave the same under all the transformations of D_{6h}, the LCAO-MO's for $1s_H$, $1s_C$, $2s_C$, and $2p_A$(the p orbitals along the C_2' axes) can be expressed in terms of the set a_1, a_2, a_3, a_4, a_5, a_6 where a_n is any A_1 orbital on carbon n or hydrogen n.

$$4A_{1g} \qquad a_1 + a_2 + a_3 + a_4 + a_5 + a_6$$

$$4E_{2g} \qquad \left\{\begin{matrix} 2a_1 - a_2 - a_3 + 2a_4 - a_5 - a_6 \\ -a_1 + 2a_2 - a_3 - a_4 + 2a_5 - a_6 \end{matrix}\right\}$$

$$4B_{1u} \qquad a_1 - a_2 + a_3 - a_4 + a_5 - a_6$$

$$4E_{1u} \qquad \left\{\begin{matrix} 2a_1 + a_2 - a_3 - 2a_4 - a_5 + a_6 \\ a_1 + 2a_2 + a_3 - a_4 - 2a_5 - a_6 \end{matrix}\right\}$$

The p orbitals on the carbons perpendicular to the C_2' axes form the other six orbitals:

$$A_{2g} \qquad p_1 + p_2 + p_3 + p_4 + p_5 + p_6$$

$$E_{2g} \qquad \left\{\begin{matrix} 2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6 \\ -p_1 + 2p_2 - p_3 - p_4 + 2p_5 - p_6 \end{matrix}\right\}$$

$$E_{1u} \qquad \left\{\begin{matrix} 2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6 \\ p_1 + 2p_2 + p_3 - p_4 - 2p_5 - p_6 \end{matrix}\right\}$$

$$B_{2u} \qquad p_1 - p_2 + p_3 - p_4 + p_5 - p_6$$

There will, of course, be mixing of orbitals of the same symmetry, with the linear combinations having the lowest energy obtained from the appropriate secular equation. In this case, it is obvious that s orbitals on hydrogen and carbon and the in-plane p orbitals on carbon can all be involved in the same bond, resulting in sp^2 hybridization on carbon.

The hybridization may be obtained more directly and with greater generality by considering the bonds of benzene rather than the atomic orbitals. The six C-C bonds each have $C_{2v}(C_2'')$ site symmetry and the six C-H bonds have $C_{2v}(C_2')$ site symmetry. Correlating the A_1 representation of each with D_{6h} yields twelve orbitals in D_{6h}.

Figure XX. Correlations of sigma bonds in benzene.

site symmetry $\longrightarrow$ molecular symmetry

C_{2v}	C_2''	D_{6h}
A_1	$\longrightarrow$	$A_{1g}+E_{2g}+B_{2u}+E_{1u}$

C_{2v}	C_2'	D_{6h}
A_1	$\longrightarrow$	$A_{1g}+E_{2g}+B_{1u}+E_{1u}$

to find the contributing orbitals on carbon we correlate the D_{6h} representations with $C_{2v}(C_2')$, the site symmetry of the carbons, and determine the orbitals of appropriate symmetry in C_{2v}.

site symmetry $\longleftarrow$ molecular symmetry

C_{2v}	C_2'	D_{6h}
A_1	$\longleftarrow$	A_{1g}
A_1+B_2	$\longleftarrow$	E_{2g}
A_1	$\longleftarrow$	B_{1u}
B_2	$\longleftarrow$	B_{2u}
A_1+B_2	$\longleftarrow$	E_{1u}

From the C_{2v} character table, the orbitals s, p_z ($z = C_2'$), d_x2, d_y2, and d_z2 correspond to A_1, while p_y and d_{yz} transform as B_2. This shows not only the expected sp^2 hybridization, but also some possible contribution from d orbitals of appropriate symmetry.

Symmetry representations for these orbitals in any subgroup of D_{6h} formed by substituting other atoms for hydrogen or otherwise reducing the symmetry of the benzene ring may be found by correlating the new symmetry with the D_{6h} representations. For example, 1,3,5 trichlorobenzene has D_{3h} symmetry with the C_2' axes of benzene retained. The correlation tables yield the following pi-orbitals:

Figure XXI. Pi-bonding orbitals in 1,3,5 trichlorobenzene.

D_{6h}	$\xrightarrow{C_2'}$	D_{3h}
B_{2g}		A_2''
E_{1g}		E''
A_{2u}		A_2''
E_{2u}		E''

Cyclobutadiene - molecular orbitals

The highest possible symmetry, D_{4h}, is assumed for the purposes of calculation. Changes in the orbitals caused by Jahn-Teller distortion or substitution are determined from the correlation tables by the method described for substituted benzenes.

The four carbon atoms in square-planar cyclobutadiene occupy equivalent $C_{2v}(C_2')$ sites, as do the four hydrogen atoms. The p-orbitals involved in pi-bonding are perpendicular to the plane of the molecule, and therefore colinear with the x-axes in C_{2v}. This corresponds to a B_1 representation in C_{2v}.

Figure XXII- pi-bonding in cyclobutadiene

$$C_{2v} \xrightarrow[C_2']{} D_{4h}$$

$$B_1 \longrightarrow E_g + A_{2u} + B_{2u}$$

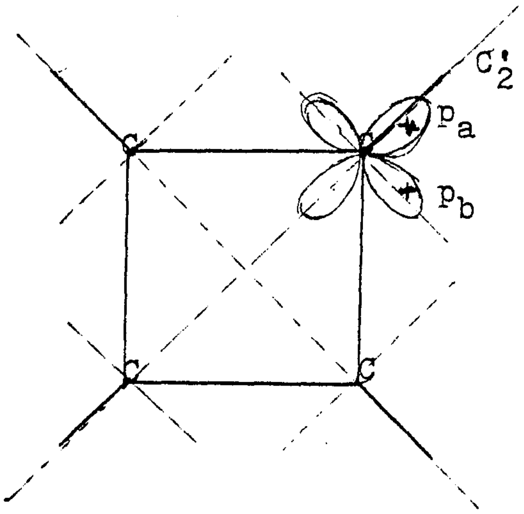
pi-bonding orbitals

$$E_g: \quad \begin{cases} p_1 - p_3 \\ p_2 - p_4 \end{cases}$$

$$\text{or} \quad \begin{cases} p_1 + p_2 - p_3 - p_4 \\ p_1 - p_2 - p_3 + p_4 \end{cases}$$

$$A_{2u}: \quad p_1 + p_2 + p_3 + p_4$$

$$B_{2u}: \quad p_1 - p_2 + p_3 - p_4$$



Sigma bonding in cyclobutadiene involves 2s, and two 2p orbitals on carbon, and the 1s orbital on the hydrogens.

Carbon orbitals:	2s	$2p_a$	$2p_b$	Hydrogen orbital:	1s
site sym. $C_{2v}(C_2')$	A_1	A_1	B_2	$C_{2v}(C_2')$	A_1

The orbitals p_a and p_b are mutually orthogonal p-orbitals on each carbon atom in the plane of the molecule. The p_a orbitals are colinear with the C_2' axes and the p_b orbitals are perpendicular, as in benzene.

As in benzene, all the A_1 orbitals transform into each other in the same manner and are represented here as a_1, a_2, a_3 and a_4.

Figure XXIII. Sigma bonding in CBD

$$
\begin{array}{lcl}
C_{2v} & \xrightarrow[C_2']{} & D_{4h} \\
3A_1 & & 3A_{1g} + 3B_{1g} + 3E_u \\
B_2 & & A_{2g} + B_{2g} + E_u
\end{array}
$$

sigma-bonding orbitals

$$
\begin{array}{llcl}
3A_{1g} & a_1 + a_2 + a_3 + a_4 & & \\
3B_{1g} & a_1 - a_2 + a_3 - a_4 & & \\
3E_u & \begin{Bmatrix} a_1 - a_3 \\ a_2 - a_4 \end{Bmatrix} & \text{or} & \begin{Bmatrix} a_1 + a_2 - a_3 - a_4 \\ a_1 - a_2 - a_3 + a_4 \end{Bmatrix} \\
A_{2g} & b_1 + b_2 + b_3 + b_4 & & \\
B_{2g} & b_1 - b_2 + b_3 - b_4 & & \\
E_u & \begin{Bmatrix} b_1 - b_3 \\ b_2 - b_4 \end{Bmatrix} & \text{or} & \begin{Bmatrix} b_1 + b_2 - b_3 - b_4 \\ b_1 - b_2 - b_3 + b_4 \end{Bmatrix}
\end{array}
$$

The representations for the pi-orbitals of CBD can be obtained by correlation of the D_{4h} orbitals into the lower symmetries:

Figure XXIV. distortions of CBD - pi-orbitals

D_{4h}	A_{2u}	B_{2u}	E_g
$D_{2h}(C_2')$	B_{1u}	B_{1u}	$B_{2g} + B_{3g}$
$D_{2h}(C_2'')$	B_{1u}	A_u	$B_{2g} + B_{3g}$
$D_{2d}(C_2'')$	B_2	A_1	E
$C_{2v}(C_2')$	B_1	B_1	$A_2 + B_1$
$C_{2v}(C_2'')$	B_1	A_2	$A_2 + B_1$

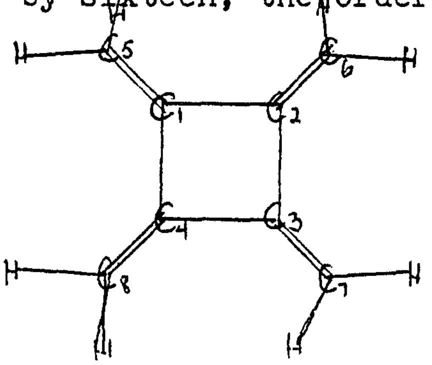
Comparison with Standard Methods

Tetramethylenecyclobutane molecular orbitals are obtained by standard methods[22] to contrast with the correlation method. Using eight p-orbitals, a reducible representation is obtained to which the pi-MO's must belong. The set of p-orbitals is operated on by each of the symmetry operations of D_{4h}, and the trace of each resulting matrix forms the characters of the reducible representation. A character will be zero unless the operation leaves some atom in the same location.

Figure XXV. Operations of D_{4h} and reducible representation of p-orbitals of tetramethylenecyclobutane.

D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Γ^{π}	8	0	0	0	-4	0	0	-8	0	4
Γ^{π}	8	0	0	-4	0	0	0	-8	4	0

The C_2' and C_2'' labels are interchanged because of the difference in convention.[23] To reduce this representation, the product with each of the irreducible representations of D_{4h} is taken and the result is divided by sixteen, the order of the group.



[22] F.A. Cotton, Chemical Applications of Group Theory, p.117.

[23] See axis conventions.

Figure XXVI. Reduction of pi-orbital representation

$$\Gamma^{\pi} x\ A_{1g} = 8+0+0-8+0+0+0-8+8+0 = 0$$

$$\Gamma^{\pi} x\ A_{2g} = 8+0+0+8+0+0+0-8-8+0 = 0$$

$$\Gamma^{\pi} x\ B_{1g} = 8+0+0-8+0+0+0-8+8+0 = 0$$

$$\Gamma^{\pi} x\ B_{2g} = 8+0+0+8+0+0+0-8-8+0 = 0$$

$$\Gamma^{\pi} x\ E_{g} = 16+0+0+0+0+0+0+16+0+0 = 32/16 = 2$$

$$\Gamma^{\pi} x\ A_{1u} = 8+0+0-8+0+0+0+8-8+0 = 0$$

$$\Gamma^{\pi} x\ A_{2u} = 8+0+0+8+0+0+0+8+8+0 = 32/16 = 2$$

$$\Gamma^{\pi} x\ B_{1u} = 8+0+0-8+0+0+0-8+8+0 = 0$$

$$\Gamma^{\pi} x\ B_{2u} = 8+0+0+8+0+0+0+8+8+0 = 32/16 = 2$$

$$\Gamma^{\pi} x\ E_{u} = 16+0+0+0+0+0+0-16+0+0 = 0$$

$$\Gamma^{\pi} = 2E_g + 2A_{2u} + 2B_{2u} \qquad \text{(III.9)}$$

This result can be obtained from the correlation tables as follows:

The inner four carbons have site symmetry $C_{2v}(C'_2)$ and the perpendicular p-orbitals belong to the B_1 representation in C_{2v}. The four outer carbons are an equivalent set with the same site symmetry and orbital representation.

Figure XXVII. Correlation method of determining pi-orbitals of tetramethylenecyclobutane

$$\begin{array}{ll} C_{2v} \xrightarrow[C'_2]{} & D_{4h} \\ \hline 2B_1 & 2A_{2u} + 2B_{2u} + 2E_g \end{array}$$

$$\Gamma^{\pi} = 2A_{2u} + 2B_{2u} + 2E_g \qquad \text{(III.10)}$$

Vibronic Coupling

The Intersection Theorem and the Correlation Method are used to find a molecular geminal of symmetry appropriate to convert a reactant ground state to a product ground state.[24] The reaction under consideration is:[25]

$$CH^+ + C_5H_5^- \longrightarrow C_6H_6 \qquad \text{(III.11)}$$

When we regard the reactants separately, CH^+ has $C_{\infty v}$ symmetry, and $C_5H_5^-$ is an aromatic system of D_{5h} symmetry. CH^+ approaches the anion with its major axis colinear to the z-axis of $C_5H_5^-$. Since the invariant points coincide, the intersection theorem may be applied:

$$C_{\infty v} \cap D_{5h} = C_{5v} \qquad \text{(III.12)}$$

In C_{5v} the geminal ground state is $^1E_2$:

$$\left.\begin{aligned} p_{x1}p_{\bar{y}2} + p_{x2}p_{\bar{y}1} &= e_{zs} \\ p_{x1}p_{\bar{x}2} - p_{y1}p_{\bar{y}2} &= e_{zc} \end{aligned}\right\} E_2 \qquad \text{(III.13)}$$

The product, C_6H_6, is considered in C_{5v} symmetry, rather than after it has rearranged to the more stable benzene D_{6h} symmetry. In C_{5v} the product ground state is $^1A_1$, resulting from the interaction of the E_2 ground state of the CH^+ geminals formed from p_x and p_y orbitals, and an appropriate vibration of the complex. The form of the vibration must be such that

$$e_{zc}\nu_{zc} + e_{zs}\nu_{zs} \text{ has } A_1 \text{ symmetry} \qquad \text{(III.14)}$$

In general terms, the interaction between ground state and vibration has the same symmetry as the product

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[24] C. Trindle, J. Am. Chem. Soc. 92, 3251-3255 (1970)
[25] C. Trindle, unpublished correspondence

ground state.

$$(\Gamma_R \times \Gamma_{q_i}) \times \Gamma_P = A_1 \qquad \text{(III.15)}$$

In this case, Γ_R, the reactant ground state, transforms as E_2, while Γ_P, the product ground state, spans A_1:

$$(E_2 \times \Gamma_{q_i}) \times A_1 = A_1 \qquad \text{(III.16)}$$

Γ_{q_i}, the representation of the vibration in C_{5v} must also be of E_2 symmetry for the product with the E_2 ground state to include A_1. To find out whether there is a vibration of E_2 symmetry, we apply the Correlation Method.

Figure XXVIII. $CH^+ + C_5H_5^-$: symmetry and ground state geminals of reactants.

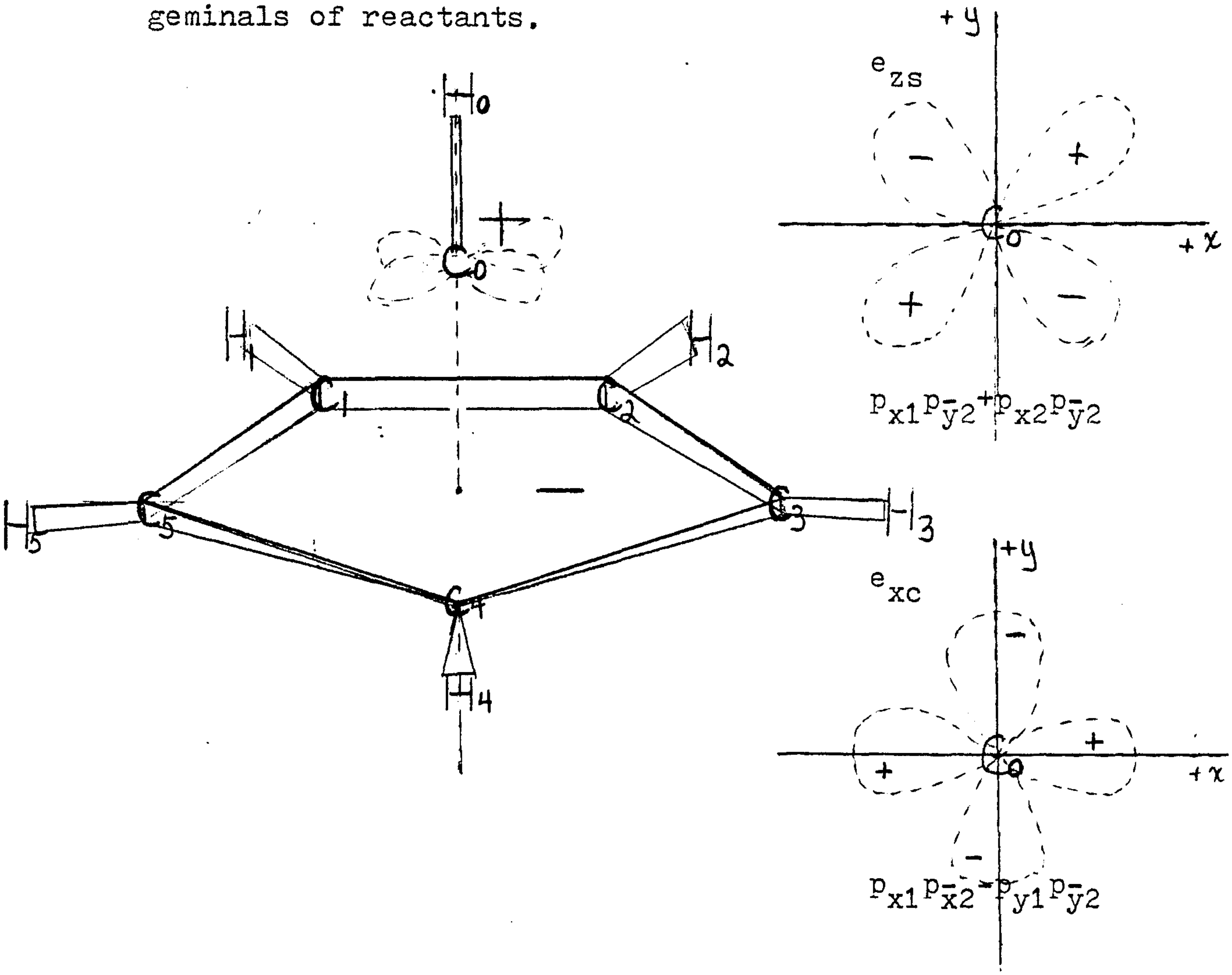


Figure XXIX. Vibrations in C_{5v}

Equivalent atoms	Site	$T_x, T_y, T_z \longrightarrow C_{5v}$	
C_0	C_{5v}	$A_1 + E$	A_1+E
H_0	C_{5v}	$A_1 + E$	A_1+E
C_1, C_2, C_3, C_4, C_5	C_s	$2A'+A''$	$2A_1+A_2+3E_1+3E_2$
H_1, H_2, H_3, H_4, H_5	C_s	$2A'+A''$	$2A_1+A_2+3E_1+3E_2$
Translations			A_1+E_1
Rotations			A_2+E_1
Vibrations			$5A_1+A_2+6E_1+6E_2$

The Correlation Method reveals the presence of six vibrations of E_2 symmetry, and also leads us to expect no contribution from CH^+ since its vibrational contribution does not correspond to the E_2 symmetry representation. The form of the vibration is now determined from the E_2 representation in C_{5v}.[26]

C_{5v}	E	$2C_5$	$2C_5^2$	$5\sigma_v$
E_2	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0

E_2 is now applied to a set of orthogonal vectors on each atom.

$$\begin{aligned} E_2(Cx_0) &= 2x_0+2\cos 144^\circ(x_0\cos 72^\circ+y_0\sin 72^\circ)+2\cos 144^\circ(y_0\cos 72^\circ \\ &\quad -x_0\sin 72^\circ)+2\cos 72^\circ(y_0\cos 144^\circ+x_0\sin 144^\circ)+2\cos 72^\circ \\ &\quad (y_0\cos 144^\circ-x_0\sin 144^\circ) \\ &= 2x_0+4x_0(-0.809)(0.309)+4x_0(0.309)(-0.809) \\ E_2(Cx_0) &= 0 = E_2(Hx_0) \qquad \text{(III.15)} \end{aligned}$$

---

26. See Appendix B

$$
\begin{aligned}
E_2(Cy_0) &= 2y_0+2\cos 144^\circ(y_0\cos 72^\circ-x_0\sin 72^\circ)+2\cos 144^\circ \\
&\quad (y_0\cos 72^\circ+x_0\sin 72^\circ)+2\cos 72^\circ(y_0\cos 144^\circ+x_0 \\
&\quad \sin 144^\circ)+2\cos 72^\circ(y_0\cos 144^\circ-x_0\sin 144^\circ) \\
&= 2y_0+4y_0(-0.809)(0.309)+4y_0(0.309)(-0.809) \\
E_2(Cy_0) &= 0 = E_2(Hy_0) \qquad \text{(III.16)}
\end{aligned}
$$

$$
\begin{aligned}
E_2(Cz_0) &= 2z_0+2\cos 144^\circ(z_0)+2\cos 144^\circ(z_0)+2\cos 72^\circ(z_0) \\
&\quad +2\cos 72^\circ(z_0) \\
&= 2z_0+4z_0(-0.809)+4z_0(0.309) \\
&= 2z_0-3.236z_0+1.236z_0 \\
E_2(Cz_0) &= 0 = E_2(Hz_0) \qquad \text{(III.17)}
\end{aligned}
$$

As predicted by the correlation method, CH^+ makes no contribution to the vibrations of E_2 symmetry.

E_2 vibrations of the $C_5H_5^-$ ring

On each atom a set of orthogonal vectors is determined. The vector z_i is perpendicular to the plane of the ring at carbon i, a_i is colinear with the C_2' axis passing through carbon i, and b_i is perpendicular to the a_i vector in the plane of the ring. A similarly defined set of vectors may be constructed on the hydrogen atoms, which transform in exactly the same manner as the corresponding z_i, a_i, and b_i vectors on the carbons.

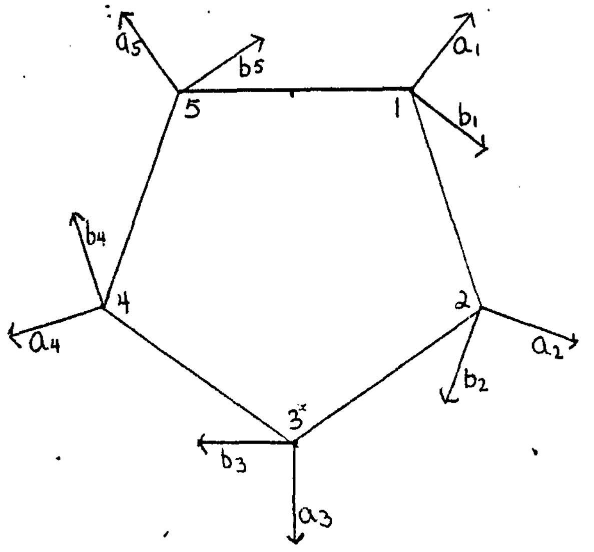
$$
\begin{aligned}
E_2(z_1) &= 2z_1+2\cos 144^\circ z_2+2\cos 144^\circ z_5+2\cos 72^\circ z_3+2\cos 72^\circ z_4 \\
&= 2z_1-2(0.809)z_2+2(0.309)z_3+2(0.309)z_4-2(0.809)z_5
\end{aligned}
$$

Similar expressions are obtained for z_2, z_3, z_4, and z_5. The sum of any four is the additive inverse of the fifth.

$$E_2(z_1) = 1.000z_1-0.809z_2+0.309z_3+0.309z_4-0.809z_5$$
$$E_2(z_2) =-0.809z_1+1.000z_2-0.809z_3+0.309z_4+0.309z_5$$
$$E_2(z_3) = 0.309z_1-0.809z_2+1.000z_3-0.809z_4+0.309z_5$$
$$E_2(z_4) = 0.309z_1+0.309z_2-0.809z_3+1.000z_4-0.809z_5$$
$$E_2(z_5) =-0.809z_1+0.309z_2+0.309z_3-0.809z_4+1.000z_5 \quad \text{(III.18)}$$

The five vibrations are indistinguishable. However, once one, for example $E_2(z_5)$ is eliminated as linearly dependent on the other four, two sets are distinguished. The vectors z_1 and z_4 are adjacent to the omitted vector, while z_2 and z_3 are not. When the sets $\{E_2(z_1)+E_2(z_4); E_2(z_1)-E_2(z_4)\}$ and $\{E_2(z_2)+E_2(z_3); E_2(z_2)-E_2(z_3)\}$ are formed, they are found to be distinguishable, while this is not true of other pairings of vectors when the sums and differences are formed. The z vectors on carbon therefore give rise to two sets of degenerate E_2 vibrations: $\{E_2(z_1),E_2(z_4)\}$ and $\{E_2(z_2),E_2(z_3)\}$.

Figure XXX. In-plane vectors of $C_5H_5^-$



The vectors a_1, a_2, a_3, a_4, a_5 and b_1, b_2, b_3, b_4, b_5 transform in the same manner as the z_i vectors for the rotational operations of C_{5v}. Since the character for the mirror planes in the E_2 representation is zero, the σ_v operations have no effect on the E_2 vibrations and the a_i's and b_i's give rise to vibrations of exactly the same form as have been determined for the z_i's.

In all, six sets of E_2 vibrations are formed:

$\{E_2(z_1), E_2(z_4)\}$ $\{E_2(z_2), E_2(z_3)\}$

$\{E_2(b_2), E_2(b_4)\}$ $\{E_2(b_2), E_2(b_3)\}$

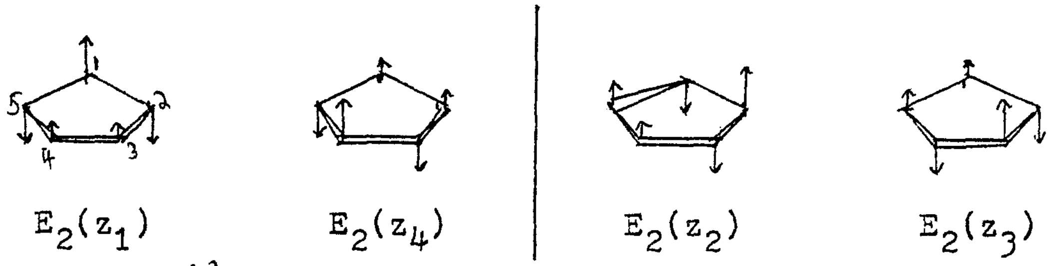
Figure XXXI. E_2 vibrations of $C_5H_5^-$

$\{E_2(z_1), E_2(z_4)\}$ out-of-plane bending

$E_2(z_1) = 1.000z_1 - 0.809z_2 + 0.309z_3 + 0.309z_4 - 0.809z_5$.

$E_2(z_1) = 1.000z_1 - 0.809z_2 + 0.309z_3 + 0.309z_4 - 0.809z_5$

$E_2(z_4) = 0.309z_1 + 0.309z_2 - 0.809z_3 + 1.000z_4 - 0.809z_5$



$E_2(z_1)$ $E_2(z_4)$ $E_2(z_2)$ $E_2(z_3)$

$\{E_2(z_2), E_2(z_3)\}$ out-of-plane bending

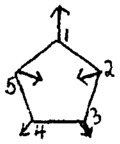
$E_2(z_2) = -0.809z_1 + 0.809z_2 - 0.809z_3 + 0.309z_4 + 0.309z_5$

$E_2(z_3) = 0.309z_1 - 0.809z_2 + 1.000z_3 - 0.809z_4 + 0.309z_5$

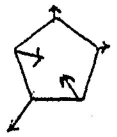
$\{E_2(a_1), E_2(a_4)\}$ in-plane angle stretching

$E_2(a_1) = 1.000a_1 - 0.809a_2 + 0.309a_3 + 0.309a_4 - 0.809a_5$

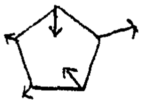
$E_2(a_4) = 0.309a_1 + 0.309a_2 - 0.809a_3 + 1.000a_4 - 0.809a_5$



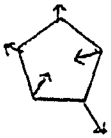
$E_2(a_1)$



$E_2(a_4)$



$E_2(a_2)$



$E_2(a_3)$

$E_2(a_2)$,$E_2(a_3)$ in-plane angle stretching

$E_2(a_2) =-0.809a_1+1.000a_2-0.809a_3+0.309a_4+0.309a_5$

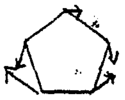
$E_2(a_3) = 0.309a_1-0.809a_2+1.000a_3-0.809a_4+0.309a_5$

$E_2(b_1)$,$E_2(b_4)$ in-plane bond stretching

$E_2(b_1) = 1.000b_1-0.809b_2+0.309b_3+0.309b_4-0.809b_5$

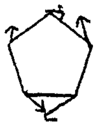
$E_2(b_4) = 0.309b_1+0.309b_2-0.809b_3+1.000b_4-0.809b_5$

$E_2(b_1)$



$E_2(b_4)$

$E_2(b_2)$



$E_2(b_3)$

$E_2(b_2)$,$E_2(b_3)$ in-plane bond stretching

$E_2(b_2) =-0.809b_1+1.000b_2-0.809b_3+0.309b_4+0.309b_5$

$E_2(b_3) = 0.309b_1-0/809b_2+1.000b_3-0.809b_4+0.309b_5$

Any of these E_2 vibrations would be appropriate symmetrically to interact with the $^1E_2$ geminal ground state to produce the required $^1A_1$ ground state of the product, and some particular combination of these would give the lowest energy. Since the eventual product is benzene, the in-plane bond stretching seems particularly promising as a major contributor towards the vibronic coupling, since one of the bonds, C_1-C_5, is stretched in both degenerate vibrations.

The direct product $E_2 \times E_2$ equals $A_1 + A_2 + E_1$. Given the basis set of geminals spanning the E_2 representation of C_{5v}, and the set of E_2 vibrations of the ring, it is known that a subset of the direct product of vibration and geminal will span A_1, the totally symmetric representation of C_{5v}.

The result of multiplying the set of geminals given by any of the E_2 sets of vibrations does not, however, span A_1:

$e_{zs}v_2 + e_{zc}v_3 = d_1(\pm 0.809e_{zs}+0.309e_{zc}) + d_2(1.000e_{zs}$
$-0.809e_{zc}) + d_3(-0.809e_{zs}+1.000e_{zc}) + d_4(0.309e_{cs}$
$-0.809e_{zc}) + d_5(0.309e_{zs}+0.309e_{zc})$

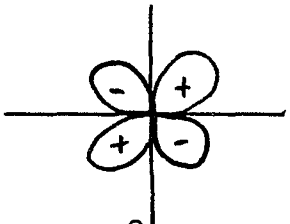
where d_i is a vector on C_i.

We consider here a product which has the form of the sum of vibration vectors each multiplied by a geminal whose mirror plane matches that of the vector in question.

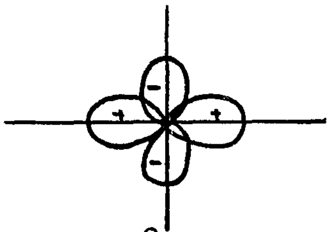
The set of geminals given differ by a rotation of 45°.

e_{zs}: x1y2+x2y1

e_{zc}: x1x2-y1y2



e_{zs}



e_{zc}

In general, any linear combination of the E_2 geminals will also span E_2; as long as one geminal is not a simple multiple of the other, the result is an E_2 set:

$$E_2 \begin{cases} m(e_{zs}) + n(e_{zc}) \\ k(e_{zs}) + q(e_{zc}) \end{cases}, \qquad m/k \neq n/q$$

We investigate here the effect of rotating the geminal set. By rotating a multiple of 72° a basis set of geminals can be formed whose mirror planes differ by the same angles as the vibrations of interest.

Rotation by θ°: $x1 \rightarrow x1\cos\theta - y1\sin\theta$

$$x2 \rightarrow x2\cos\theta - y2\sin\theta$$

$$y1 \rightarrow y1\cos\theta + x1\sin\theta$$

$$y_2 \rightarrow y_2\cos\theta + x_2\sin\theta$$

$$e_{zs} = x_1y_2 + x_2y_1$$

$$\begin{aligned} R\theta(e_{zs}) &= (x_1\cos\theta-y_1\sin\theta)(y_2\cos\theta+x_2\sin\theta) + (x_2\cos\theta \\ &\quad -y_2\sin\theta)(y_1\cos\theta+x_1\sin\theta) \\ &= \sin\theta\cos\theta x_1x_2-\sin\theta\cos\theta y_1y_2+\cos^2\theta x_1y_2-\sin^2\theta x_2y_1 \\ &\quad \underline{+\sin\theta\cos\theta x_1x_2-\sin\theta\cos\theta y_1y_2-\sin^2\theta x_1y_2+\cos^2\theta x_2y_1} \\ &=2\sin\theta\cos\theta(x_1x_2-y_1y_2) + (\cos^2\theta-\sin^2\theta)(x_1y_2-x_2y_1) \\ &= \sin2\theta\,(e_{zc}) + \cos2\theta\,(e_{zs}) \end{aligned}$$

Thus the rotation of e_{zs} by any angle results in a linear combination of e_{zs} and e_{zc}. The set

$$e_{zs},\ \sin2\theta\,(e_{zc}) + \cos2\theta\,(e_{zs})$$

spans E_2 unless $\sin2\theta = 0$. ($\theta = 90^{\circ}$ or multiple).

In particular, for rotations of 72° and 144°, the angles separating the mirror planes of the vibrations, E_2 sets are formed:

$$E_2 \begin{cases} e_{zs} \\ R72^{\circ}(e_{zs})=0.588e_{zc}-0.809e_{zs} \end{cases}$$

$$E_2 \begin{cases} e_{zs} \\ R216^{\circ} \end{cases}$$

Consider the subset of $E_2 x E_2$ formed by multiplying a vibration by a geminal set with matching mirror planes:

$$S = v_1 e_{zs} - v_4 R216^{\circ}(e_{zs})$$

$$S = (1.000d_1 - 0.809d_2 + 0.309d_3 + 0.309d_4 - 0.809d_5)e_{zs}$$
$$- (0.309d_d + 0.309d_2 - 0.809d_3 + 1.000d_4 - 0.809d_5)(0.309e_{zs} + 0.951e_{zc})$$

$$S = d_1(o.905e_{zs} - 0.294e_{zc}) + d_2(-0.905e_{zs} - 0.294e_{zc})$$
$$+ d_3(0.559e_{zs} + 0.769e_{zc}) + d_4(-0.951e_{zc}) + d_5(-0.559e_{zs} + 0.769e_{zc})$$

Dividing through by -0.951, the coefficient of $d_4 e_{zc}$, clarifies the results:

$$S = d_1(-0.951e_{zs} + 0.309e_{zc}) + d_2(0.951e_{zs} + 0.309e_{zc})$$
$$+ d_3(-0.588e_{zs} - 0.809e_{zc}) + d_4 e_{zc} + d_5(0.588e_{zs} - 0.809e_{zc})$$

Comparing these results with the rotations of e_{zc}, obtained by the same method as those of e_{zs}:

$$e_{zc} = x_1 x_2 - y_1 y_2$$

$$R\,\theta(e_{zc}) = -\sin 2\theta(e_{zs}) + \cos 2\theta(e_{zc})$$

$$R72^{\circ} e_{zc} = -0.588e_{zs} - 0.809e_{zc}$$

$$R144^{\circ} e_{zc} = 0.951e_{zs} + 0.309e_{zs}$$

$$R216^{\circ} e_{zc} = -0.951e_{zs} + 0.309e_{zc}$$

$$R288^{\circ} e_{zc} = 0.588e_{zs} - 0.809e_{zc}$$

We may then rewrite S in terms of rotations of e_{zc}:

$$S = d_1 R216^{\circ} e_{zc} + d_2 R144^{\circ} e_{zc} + d_3 R72^{\circ} e_{zc} + d_4 e_{zc} + d_5 R288^{\circ} e_{zc}$$

This subset of the product is apparently of A_1 symmetry. To check this, we strike it with the A_1 operator .(It is sufficient to consider C_5, rather than C_{5v})

$E(S) = d_1R216^\circ e_{zc} + d_2R144^\circ e_{zc} + d_3R72^\circ e_{zc} + d_4e_{zc} + d_5R288^\circ e_{zc}$

$C_5(S) = d_1R216^\circ e_{zc} + d_2R144^\circ e_{zc} + d_3R72^\circ e_{zc} + d_4e_{zc} + d_5R288^\circ e_{zc}$

$C_5(S) = C_5^2(S) = C_5^3(S) = C_5^4(S)$

$A_1(S) = (E(S) + C_5(S) + C_5^2(S) + C_5^3(S) + C_5^4(S))1/5$

$A_1(S) = \frac{1}{5}(5d_1R216^\circ e_{zc} + 5d_2R144^\circ e_{zc} + 5d_3R72^\circ e_{zc} + 5d_4e_{zc} + 5d_5R288^\circ e_{zc})$

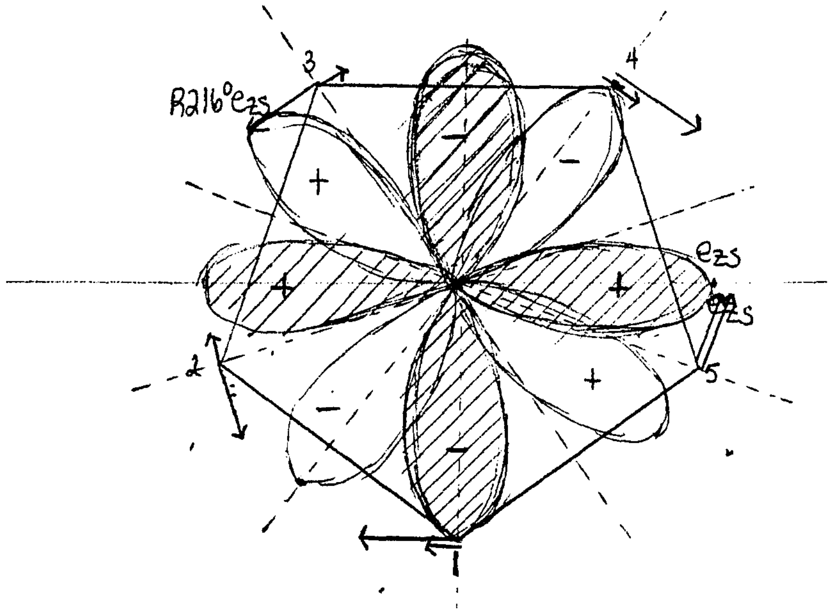
$A_1(S) = S$

Thus it has been shown that the product

$$v_1e_{zs} - v_4R216^\circ e_{zs}$$

is of A_1 symmetry.

Figure XXXII. Superimposed symmetry-oriented geminals and ring vibrations.



Axis Conventions

Fateley[27] and Cotton[28] differ in nomenclature regarding C_2' and C_2'' axes. In this work Fateley is followed so that C_2' axes pass through two equivalent atoms on opposite sides of the molecule, while C_2'' axes bisect opposite bonds. Correspondingly, σ_v mirror planes include a C_2' axis and the major axis, while σ_d mirror planes include C_2'' and the major axis. In Cotton the conventions are reversed.

Although the character tables are identical in Fateley and Cotton, this difference in nomenclature gives rise to different irreducible representations in certain cases. For example, in benzene (D_{6h}) the irreducible representation B_{1g} has the character +1 with respect to reflection through σ_d and -1 with respect to σ_v. In B_{2g}, these characters are reversed, as are those of the C_2' and C_2'' axes.

Consider the pi-bonding orbital of benzene:

$$\Gamma_\pi = p_1 - p_2 + p_3 - p_4 + p_5 - p_6$$

In Cotton, this orbital would belong to B_{1g}, while in Fateley it corresponds to B_{2g}.

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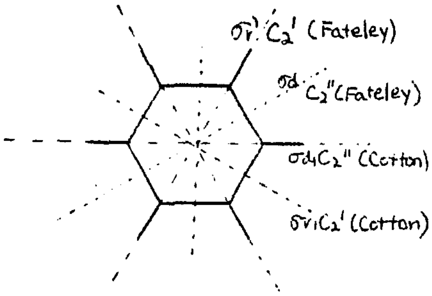
[27] W.G. Fateley, op. cit.
[28] F.A. Cotton, op. cit.

Figure XXXIII. Benzene - axis conventions



Examples drawn from Cotton and other sources using his convention are translated into Fateley's nomenclature to allow comparison between conventional results and those of the Correlation Method.

Another crucial convention concerns location of x, y and z axes. All sources agree in establishing z as the major axis. However, in the correlations $D_{4h} \xrightarrow[C_2']{} C_{2v}$ and $D_{4h} \xrightarrow[C_2'']{} C_{2v}$, the y axis appears to have been chosen as perpendicular to the plane of the molecule in the C_{2v} site symmetries. To conform to standard usage, the tables have been amended by reversing B_1 and B_2 in these correlations. B_1 is the representation thet transforms as the x-axis, while the y-axis transforms as B_2.

Appendix A - Summary of Crystal Properties[29]

All vectors in groups (ii) to (vi) are polar, except for the vectors H, B and I, which are taken as axial.

Property or coefficients	Defining equation
(i) Scalar relating two scalars	
heat capacity C	$\Delta S = (C/T)\Delta T$
(ii) 1st-rank tensor relating a scalar and a vector	
pyroelectricity	$\Delta P_i = p_i \Delta T$
electrocaloric effect	$\Delta S = p_i E_i$
heat of polarization	$\Delta S = t_i \Delta P_i$
field due to temperature change	$E_i = -t_i \Delta T$
polarization by hydrostatic pres.	$P_i = -d_{ijj} p$
(iii) 2nd-rank tensor ralating two vectors	
permittivity	$D_i = \kappa_{ij} E_j$
dielectric impermeability	$E_i = \beta_{ij} D_j$
dielectric susceptibility	$P_i = \kappa_0 \chi_{ij} E_j$
permeability	$B_i = \mu_{ij} H_j$
magnetic susceptibility	$I_i = \mu_0 \psi_{ij} H_j$
electrical conductivity	$j_i = \sigma_{ik} E_k$
electrical resistivity	$E_i = \rho_{ik} j_k$
thermal conductivity	$h_i = -k_{ij}(\partial T/\partial x_k)$
thermal resistivity	$\partial T/\partial x_i = -r_{ij} h_j$
thermoelectricity	$\partial \bar{\mu}/\partial x_i = -\Sigma_{ik}(\partial T/\partial x_k)$ (not symmetrical)

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[29] J.F. Nye, op. cit.

(iv) 2nd -rank tensor relating a scalar and a second rank tensor

thermal expansion	$\epsilon_{ij} = \alpha_{ij} \Delta T$
piezocaloric effect	$\Delta S = \alpha_{ij} \sigma_{ij}$
thermal pressure	$\sigma_{ij} = -f_{ij} \Delta T$
heat of deformation	$\Delta S = f_{ij} \epsilon_{ij}$
strain by hydrostatic pressure	$\epsilon_{ij} = -s_{ijkk} p$
Peltier coefficients	$\Pi_{ik} = (T/e) \Sigma_{ik}$

(v) 3rd-rank tensor relating a vector and a 2nd-rank tensor

direct piezoelectric effect	$P_i = d_{ijk} \sigma_{jk}$
converse piezoelectric effect	$\epsilon_{jk} = d_{ijk} E_i$
a piezoelectric effect	$\sigma_{jk} = -e_{ijk} E_i$
a piezoelectric effect	$P_i = e_{ijk} \epsilon_{jk}$
electro-optical effect	$\Delta B_{ij} = z_{ijk} E_k$

(vi) 4th-rank tensor relating two 2nd-rank tensors

elastic compliances	$\epsilon_{ij} = s_{ijkl} \sigma_{kl}$
elastic stiffness	$\sigma_{ij} = c_{ijkl} \epsilon_{kl}$
elasto-optical coefficients	$\Delta B_{ij} = p_{ijkl} \epsilon_{kl}$
piezo-optical coefficients	$\Delta B_{ij} = \pi_{ijkl} \sigma_{kl}$
electrostriction	$\epsilon_{jk} = \gamma_{iljk} E_i E_i$

(vii) Axial 2nd-rank tensor giving the variation of a pseudo-scalar with direction

optical activity (gyration vector)	$G = g_{ij} l_i l_j$

Appendix B Character Tables

The species of the translations x, y, and z and the rotations R_x, R_y, and R_z in a right-handed system parallel to the x, y, and z axes, respectively, are given for each point group. Also, the species of the polarization tensor elements, α_{ij}, is identified for each point group. This allows us to determine immediately the spectral activity of each species in a point group; for example, all those species that contain a translation will be infrared active, whereas those species containing an element of the polarization tensor α_{ij} will have Raman activity.

C_s	E	σ_h		
A'	1	1	$T_x, T_y; R_z$	xx, yy, zz, xy
A"	1	-1	$T_z; R_x, R_y$	xz, yz

C_i	E	i		
A_g	1	1	R_x, R_y, R_z	xx, yy, zz, xy, xz, yz
A_u	1	-1	T_x, T_y, T_z	

C_2	E	C_2		
A	1	1	$T_z; R_z$	xx, yy, zz, xy
B	1	-1	$T_x, T_y; R_x, R_y$	xz, yz

C_{2h}	E	C_2	i	σ_h		
A_g	1	1	1	1	R_z	xx, yy, zz, xy
B_g	1	-1	1	-1	R_x, R_y	xz. yz
A_u	1	1	-1	-1	T_z	
B_u	1	-1	-1	1	T_x, T_y	

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	T_z	xx, yy, zz
A_2	1	1	-1	-1	R_z	xy

C_{2v}	E	C_2	σ_v	σ_v'		
A_1	1	1	1	1	T_z	xx,yy,zz
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	$T_x;R_y$	xz
B_2	1	-1	-1	1	$T_y;R_x$	yz

D_2	E	$C_2(z)$	$C_2(y)$	$C_2(x)$		
A	1	1	1	1		xx,yy,zz
B_1	1	1	-1	-1	$T_z;R_z$	xy
B_2	1	-1	1	-1	$T_y;R_y$	xz
B_3	1	-1	-1	1	$T_x;R_x$	yz

D_{2d}	E	$2S_4$	C_2	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		xx-yy
B_2	1	-1	1	-1	1	T_z	xy
E	2	0	-2	0	0	(T_x,T_y); (R_x,R_y)	xz,yz

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(zx)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		xx,yy,zz
B_{1g}	1	1	-1	-1	1	1	-1	-1	R_z	xy
B_{2g}	1	-1	1	-1	1	-1	1	-1	R_y	xz
B_{3g}	1	-1	-1	1	1	-1	-1	1	R_x	yz
A_u	1	1	1	1	-1	-1	-1	-1		
B_{1u}	1	1	-1	-1	-1	-1	1	1	T_z	
B_{2u}	1	-1	1	-1	-1	1	-1	1	T_y	
B_{3u}	1	-1	-1	1	-1	1	1	-1	T_x	

$\varepsilon = e^{2\pi i/3}$

C_3	E	C_3	C_3^2		
A	1	1	1	$T_z;R_z$	xx+yy,zz
E	$\left\{\begin{matrix}1\\1\end{matrix}\right.$	$\begin{matrix}\varepsilon\\\varepsilon^*\end{matrix}$	$\left.\begin{matrix}\varepsilon^*\\\varepsilon\end{matrix}\right\}$	$(T_x,T_y);(R_x,R_y)$	(xx-yy,xy),(xz,yz)

C_{3h}	E	C_3	C_3^2	o_h	S_3	S_3^5		$= e^{2\ i/3}$
A'	1	1	1	1	1	1	R_z	xx+yy,zz
E'	1		*	1		*	(T_x,T_y)	(xx-yy,xy)
	1	*		1	*			
A"	1	1	1	-1	-1	-1	T_z	
E"	1		*	-1	-	- *	(R_x,R_y)	(xz,yz)
	1	*		-1	- *	-		

C_{3v}	E	$2C_3$	$3o_v$		
A_1	1	1	1	T_z	xx+yy,zz
A_2	1	1	-1	R_z	
E	2	-1	0	(Tx,Ty);(R_x,R_y)	(xx-yy,xy),(xz,yz)

D_3	E	$2C_3$	$3C_2$		
A_1	1	1	1		xx+yy,zz
A_2	1	1	-1	$T_z;R_z$	
E	2	-1	0	$(T_x,T_y);(R_x,R_y)$	(xx-yy,xy),(xz,yz)

D_{3d}	E	$2C_3$	$3C_2$	i	$2S_6$	$3o_d$		
A_{1g}	1	1	1	1	1	1		xx+yy,zz
A_{2g}	1	1	-1	1	1	-1	R_z	
E_g	2	-1	0	2	-1	0	(R_x,R_y)	(xx-yy,xy),(xz,yz)
A_{1u}	1	1	1	-1	-1	-1		
A_{2u}	1	1	-1	-1	-1	1	T_z	
E_u	2	-1	0	-2	1	0	(T_x,T_y)	

D_{3h}	E	$2C_3$	$3C_2$	o_h	$2S_3$	$3o_v$		
A_1'	1	1	1	1	1	1		(xx+yy,zz)
A_2'	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	(T_x,T_y)	(xx-yy,xy)
A_1''	1	1	1	-1	-1	-1		
A_2''	1	1	-1	-1	-1	1	T_z	
E"	2	-1	0	-2	1	0	(R_x,R_y)	(xz,yz)

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	$T_z;R_z$	xx+yy,zz
B	1	-1	1	-1		xx-yy,xy
E	1	i	-1	-i	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
	1	-i	-1	i		

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	xx+yy,zz
B_g	1	-1	1	-1	1	-1	1	-1		xx-yy,xy
E_g	1	i	-1	-i	1	i	-1	-i	(R_x,R_y)	(xz,yz)
	1	-i	-1	i	1	-i	-1	i		
A_u	1	1	1	1	-1	-1	-1	-1	T_z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	1	i	-1	-i	-1	-i	1	i	(T_x,T_y)	
	1	-i	-1	i	-1	i	1	-i		

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	xx+yy,zz
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		xx-yy
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	-1	-1	$T_z;R_z$	
B_1	1	-1	1	1	-1		xx-yy
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	T_z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(T_x,T_y)	
E_2	2	0	-2	0	2	0	0		(xx-yy,xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0		

C_4	E	C_4	C_2	C_4^3		
A	1	1	1	1	T_z;R_z	xx+yy,zz
B	1	-1	1	-1		xx-yy,xy
E	1	i	-1	-i	(T_x,T_y);(R_x,R_y)	(xz,yz)
	1	-i	-1	i		

C_{4h}	E	C_4	C_2	C_4^3	i	S_4^3	σ_h	S_4		
A_g	1	1	1	1	1	1	1	1	R_z	xx+yy,zz
B_g	1	-1	1	-1	1	-1	1	-1		xx-yy,xy
E_g	1	i	-1	-i	1	i	-1	-i	(R_x,R_y)	(xz,yz)
	1	-i	-1	i	1	-i	-1	i		
A_u	1	1	1	1	-1	-1	-1	-1	T_z	
B_u	1	-1	1	-1	-1	1	-1	1		
E_u	1	i	-1	-i	-1	-i	1	i	(T_x,T_y)	
	1	-i	-1	i	-1	i	1	-i		

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$		
A_1	1	1	1	1	1	T_z	xx+yy,zz
A_2	1	1	1	-1	-1	R_z	
B_1	1	-1	1	1	-1		xx-yy
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(T_x,T_y);(R_x,R_y)	(xz,yz)

D_4	E	$2C_4$	C_2	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	-1	-1	T_z;R_z	
B_1	1	-1	1	1	-1		xx-yy
B_2	1	-1	1	-1	1		xy
E	2	0	-2	0	0	(T_x,T_y);(R_x,R_y)	(xz,yz)

D_{4d}	E	$2S_8$	$2C_4$	$2S_8^3$	C_2	$4C_2'$	$4\sigma_d$		
A_1	1	1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	1	-1		
B_2	1	-1	1	-1	1	-1	1	T_z	
E_1	2	$\sqrt{2}$	0	$-\sqrt{2}$	-2	0	0	(T_x,T_y)	
E_2	2	0	-2	0	2	0	0		(xx-yy,xy)
E_3	2	$-\sqrt{2}$	0	$\sqrt{2}$	-2	0	0		

C_{5h}	E	C_5	C_5^2	C_5^3	C_5^4	σ_h	S_5	S_5^7	S_5^8	S_5^9		$\varepsilon = e^{2\pi i/5}$
A'	1	1	1	1	1	1	1	1	1	1	R_z	xx+yy,zz
E_1'	1	ε	ε^2	ε^{2*}	ε^*	1	ε	ε^2	ε^{2*}	ε^*	(T_x,T_y)	
	1	ε^*	ε^{2*}	ε^2	ε	1	ε^*	ε^{2*}	ε^2	ε		
E_2'	1	ε^2	ε^*	ε	ε^{2*}	1	ε^2	ε^*	ε	ε^{2*}		(xx-yy,xy
	1	ε^{2*}	ε	ε^*	ε^2	1	ε^{2*}	ε	ε^*	ε^2		
A''	1	1	1	1	1	-1	-1	-1	-1	-1	T_z	
E_1''	1	ε	ε^2	ε^{2*}	ε^*	-1	$-\varepsilon$	$-\varepsilon^2$	$-\varepsilon^{2*}$	$-\varepsilon^*$	(R_x,R_y)	(xz,yz
	1	ε^*	ε^{2*}	ε^2	ε	-1	$-\varepsilon^*$	$-\varepsilon^{2*}$	$-\varepsilon^2$	$-\varepsilon$		
E_2''	1	ε^2	ε^*	ε	ε^{2*}	-1	$-\varepsilon^2$	$-\varepsilon^*$	$-\varepsilon$	$-\varepsilon^{2*}$		
	1	ε^{2*}	ε	ε^*	ε^2	-1	$-\varepsilon^{2*}$	$-\varepsilon$	$-\varepsilon^*$	$-\varepsilon^2$		

D_5	E	$2C_5$	$2C_5^2$	$5C_2$		
A_1	1	1	1	1		xx+yy,zz
A_2	1	1	1	-1	$T_z;R_z$	
E_1	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
E_2	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		(xx-yy,xy)

D_{5d}	E	$2C_5$	$2C_5^2$	$5C_2$	i	$2S_{10}^3$	$2S_{10}$	$5\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1		xx+yy,zz
A_{2g}	1	1	1	-1	1	1	1	-1	R_z	
E_{1g}	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	(R_x,R_y)	(xz,yz)
E_{2g}	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		(xx-yy,xy)
A_{1u}	1	1	1	1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	1	T_z	
E_{1u}	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	-2	$-2\cos 72^\circ$	$-2\cos 144^\circ$	0	(T_x,T_y)	
E_{2u}	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	-2	$-2\cos 144^\circ$	$-2\cos 72^\circ$	0		

D_{5h}	E	$2C_5$	$2C_5^2$	$5C_2$	σ_h	$2S_5$	$2S_5^3$	$2\sigma_v$		
A_1'	1	1	1	1	1	1	1	1		xx+yy,zz
A_2'	1	1	1	-1	1	1	1	-1	R_z	
E_1'	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	(T_x,T_y)	
E_2'	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0		(xx-yy,xy)
A_1''	1	1	1	1	-1	-1	-1	-1		
A_2''	1	1	1	-1	-1	-1	-1	1	T_z	
E_1''	2	$2\cos 72^\circ$	$2\cos 144^\circ$	0	-2	$-2\cos 72^\circ$	$-2\cos 144^\circ$	0	(R_x,R_y)	(xz,yz)
E_2''	2	$2\cos 144^\circ$	$2\cos 72^\circ$	0	-2	$-2\cos 144^\circ$	$-2\cos 72^\circ$	0		

C_6	E	C_6	C_3	C_2	C_3^2	C_6^5		$\varepsilon = e^{2\pi i/6}$
A	1	1	1	1	1	1	$T_z;R_z$	xx+yy,zz
B	1	-1	1	-1	1	-1		
E_1	1 1	ε ε^*	$-\varepsilon^*$ $-\varepsilon$	-1 -1	$-\varepsilon$ $-\varepsilon^*$	ε^* ε	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
E_2	1 1	$-\varepsilon^*$ $-\varepsilon$	$-\varepsilon$ $-\varepsilon^*$	1 1	$-\varepsilon^*$ $-\varepsilon$	$-\varepsilon$ $-\varepsilon^*$		(xx-yy,xy)

C_{6v}	E	$2C_6$	$2C_3$	C_2	$3\sigma_v$	$3\sigma_d$		
A_1	1	1	1	1	1	1	T_z	xx+yy,zz
A_2	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
E_2	2	-1	-1	2	0	0		(xx-yy,xy)

D_6	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$		
A_1	1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	1	-1	-1	$T_z;R_z$	
B_1	1	-1	1	-1	1	-1		
B_2	1	-1	1	-1	-1	1		
E_1	2	1	-1	-2	0	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
E_2	2	-1	-1	2	0	0		(xx-yy,xy)

D_{6d}	E	$2S_{12}$	$2C_6$	$2S_4$	$2C_3$	$2S_{12}^5$	C_2	$6C_2'$	$6\sigma_d$		
A_1	1	1	1	1	1	1	1	1	1		xx+yy,zz
A_2	1	1	1	1	1	1	1	-1	-1	R_z	
B_1	1	-1	1	-1	1	-1	1	-1	-1		
B_2	1	-1	1	-1	1	-1	1	-1	1	T_z	
E_1	2	$\sqrt{3}$	1	0	-1	$-\sqrt{3}$	-2	0	0	(T_x,T_y)	
E_2	2	1	-1	-2	1	2	0	0	0		(xx-yy,xy)
E_3	2	0	-2	0	2	0	-2	0	0		
E_4	2	-1	-1	2	-1	-1	2	0	0		
E_5	2	$-\sqrt{3}$	1	0	-1	$\sqrt{3}$	-2	0	0	(R_x,R_y)	(xz,yz)

$\varepsilon = e^{2\pi i/6}$

C_{6h}	E	$C_6(z)$	C_3	C_2	C_3^2	C_6^5	i	S_3^5	S_6^5	σ_h	S_6	S_3		
A_g	1	1	1	1	1	1	1	1	1	1	1	1	R_z	xx+yy,zz
B_g	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
E_{1g}	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	(R_x,R_y)	(xz,yz)
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε		
E_{2g}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	ε	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$		(xx-yy,xy)
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$		
A_u	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1	T_z	
B_u	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
E_{1u}	1	ε	$-\varepsilon^*$	-1	$-\varepsilon$	ε^*	-1	$-\varepsilon$	ε^*	1	ε	$-\varepsilon^*$	(T_x,T_y)	
	1	ε^*	$-\varepsilon$	-1	$-\varepsilon^*$	ε	-1	$-\varepsilon^*$	ε	1	ε^*	$-\varepsilon$		
E_{2u}	1	$-\varepsilon^*$	$-\varepsilon$	1	$-\varepsilon^*$	$-\varepsilon$	-1	ε^*	ε	-1	ε^*	ε		
	1	$-\varepsilon$	$-\varepsilon^*$	1	$-\varepsilon$	$-\varepsilon^*$	-1	ε	ε^*	-1	ε	ε^*		

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$		
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1		xx+yy,zz
A_{2g}	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R_z	
B_{1g}	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B_{2g}	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(Rx,Ry)	(xz,yz)
E_{2g}	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(xx-yy,xy)
A_{1u}	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	T_z	
B_{1u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
E_{1u}	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(T_x,T_y)	
B_{2u}	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

S_6	E	C_3	C_3^2	i	S_6^5	S_6		$\varepsilon = e^{2\pi i/3}$
A_g	1	1	1	1	1	1	R_z	xx+yy,zz
E_g	$\begin{cases}1\\1\end{cases}$	ε ε^*	ε^* ε	1 1	ε ε^*	ε^* ε	(R_x,R_y)	(xx-yy,xy),(xz,yz)
A_u	1	1	1	-1	-1	-1	T_z	
E_u	$\begin{cases}1\\1\end{cases}$	ε ε^*	ε^* ε	-1 -1	$-\varepsilon$ $-\varepsilon^*$	$-\varepsilon^*$ $-\varepsilon$	(T_x,T_y)	

S_8	E	S_8	C_4	S_8^3	C_2	S_8^5	C_4^3	S_8^7		$\varepsilon = e^{2\pi i/8}$
A	1	1	1	1	1	1	1	1	R_z	xx+yy,zz
B	1	-1	1	-1	1	-1	1	-1	T_z	
E_1	$\begin{cases}1\\1\end{cases}$	ε ε^*	i $-i$	$-\varepsilon^*$ $-\varepsilon$	-1 -1	$-\varepsilon$ $-\varepsilon^*$	$-i$ i	ε^* ε	(T_x,T_y); (R_x,R_y)	
E_2	$\begin{cases}1\\1\end{cases}$	i $-i$	-1 -1	$-i$ i	1 1	i $-i$	-1 -1	$-i$ i		(xx-yy,xy)
E_3	$\begin{cases}1\\1\end{cases}$	$-\varepsilon^*$ $-\varepsilon$	$-i$ i	ε ε^*	-1 -1	ε^* ε	i $-i$	$-\varepsilon$ $-\varepsilon^*$		(xz,yz)

$C_{\infty v}$	E	$2C_\infty^\phi$	$\cdots$	$\infty\sigma_v$		
$A_1=\Sigma^+$	1	1	$\cdots$	1	T_z	xx+yy,zz
$A_2=\Sigma^-$	1	1	$\cdots$	-1	R_z	
$E_1=\Pi$	2	$2\cos\phi$	$\cdots$	0	$(T_x,T_y);(R_x,R_y)$	(xz,yz)
$E_2=\Delta$	2	$2\cos2\phi$	$\cdots$	0		(xx-yy,xy)
$E_3=\Phi$	2	$2\cos3\phi$	$\cdots$	0		
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$		

$D_{\infty h}$	E	$2C_\infty^\phi$	$\cdots$	$\infty\sigma_v$	i	$2S_\infty^\phi$	$\cdots$	∞C_2		
Σ_g^+	1	1	$\cdots$	1	1	1	$\cdots$	1		xx+yy+zz
Σ_g	1	1	$\cdots$	1	1	1	$\cdots$	-1	R_z	
Π_g	2	$2\cos\phi$	$\cdots$	0	2	$-2\cos\phi$	$\cdots$	0	(R_x,R_y)	(xz,yz)
Δ_g	2	$2\cos2\phi$	$\cdots$	0	2	$2\cos2\phi$	$\cdots$	0		(xx-yy,xy)
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$		
Σ_u^+	1	1	$\cdots$	1	-1	-1	$\cdots$	-1	T_z	
Σ_u	1	1	$\cdots$	-1	-1	-1	$\cdots$	1		
Π_u	2	$2\cos\phi$	$\cdots$	0	-2	$2\cos\phi$	$\cdots$	0	(T_x,T_y)	
Δ_u	2	$2\cos2\phi$	$\cdots$	0	-2	$-2\cos2\phi$	$\cdots$	0		
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$		

T	E	$4C_3$	$4C_3^2$	$3C_2$		$\mathcal{E} = e^{2\pi i/3}$
A	1	1	1	1		xx+yy+zz
E	1	$\mathcal{E}$	$\mathcal{E}^*$	1		(xx+yy-2zz,xx-yy)
	1	$\mathcal{E}^*$	$\mathcal{E}$	1		
F	3	0	0	-1	(T_x,T_y,T_z); (R_x,R_y,R_z)	(xy,xz,yz)

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
A_1	1	1	1	1	1		xx+yy+zz
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		(xx+yy-2zz,xx-yy)
F_1	3	0	-1	1	-1	(R_x,R_y,R_z)	
F_2	3	0	-1	-1	1	(T_x,T_y,T_z)	(xy,xz,yz)

T_h	E	$4C_3$	$4C_3^2$	$3C_2$	i	$4S_6$	$4S_6^5$	$3o_h$		$\mathcal{E} = e^{2\pi i/3}$
A_g	1	1	1	1	1	1	1	1		xx+yy+zz
E_g	1	$\mathcal{E}$	$\mathcal{E}$	1	1	$\mathcal{E}$	$\mathcal{E}^*$	1		(xx+yy-2zz,xx-yy)
	1	$\mathcal{E}$	$\mathcal{E}$	1	1	$\mathcal{E}^*$	$\mathcal{E}$	1		
F_g	3	0	0	-1	3	0	0	-1	(R_x,R_y,R_z)	(xy,xz,yz)
A_u	1	1	1	1	-1	-1	-1	-1		
E_u	1	$\mathcal{E}$	$\mathcal{E}^*$	1	-1	$-\mathcal{E}^*$	$-\mathcal{E}^*$	-1		
	1	$\mathcal{E}^*$	$\mathcal{E}$	1	-1	$\mathcal{E}^*$	$-\mathcal{E}$	-1		
F_u	3	0	0	-1	-3	0	0	1		

O	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$		
A_1	1	1	1	1	1		xx+yy+zz
A_2	1	1	1	-1	-1		
E	2	-1	2	0	0		(xx+yy-2zz,xx-yy)
F_1	3	0	-1	1	-1	(T_x,T_y,T_z); (R_x,R_y,R_z)	
F_2	3	0	-1	-1	1		(xy,xz,yz)

D_{6h}	D_6	D_{3h}	D_{3h}	C_{6v}	C_{6h}	D_{3d}	D_{3d}	D_{2h}	C_6	C_{3h}
B_{1u}	B_1	A_1'	A_2'	B_1	B_u	A_{1u}	A_{2u}	B_{2u}	B	A'
B_{2u}	B_2	A_2'	A_1'	B_2	B_u	A_{2u}	A_{1u}	B_{3u}	B	A'
E_{1u}	E_1	E'	E'	E_1	E_{1u}	E_u	E_u	$B_{2u}+B_{3u}$	E_1	E'
E_{2u}	E_2	E''	E''	E_2	E_{2u}	E_u	E_u	A_u+B_{1u}	E_2	E''

D_{6h}	C_2' D_3	C_2'' D_3	σ_v C_{3v}	σ_d C_{3v}	S_6	D_2	C_2 C_{2v}	C_2' C_{2v}	C_2'' C_{2v}	C_2 C_{2h}	C_2' C_{2h}	C_2'' C_{2h}
A_{1g}	A_1	A_1	A_1	A_1	A_g	A	A_1	A_1	A_1	A_g	A_g	A_g
A_{2g}	A_2	A_2	A_2	A_2	A_g	B_1	A_2	B_2	B_1	A_g	B_g	B_g
B_{1g}	A_1	A_2	A_2	A_2	A_g	B_2	B_1	A_2	B_2	B_g	A_g	B_g
B_{2g}	A_2	A_1	A_1	A_2	A_g	B_3	B_2	B_1	A_2	B_g	B_g	A_g
E_{1g}	E	E	E	E	E_g	B_2+B_3	B_1+B_2	A_2+B_1	B_2+A_2	$2B_g$	A_g+B_g	A_g+B_g
E_{2g}	E	E	E	E	E_g	$A+B_1$	A_1+A_2	A_1+B_2	A_1+B_1	$2A_g$	A_g+B_g	A_g+B_g
A_{1u}	A_1	A_1	A_2	A_2	A_u	A	A_2	A_2	A_2	A_u	A_u	A_u
A_{2u}	A_2	A_2	A_1	A_1	A_u	B_1	A_1	B_1	B_2	A_u	B_u	B_u
B_{1u}	A_1	A_2	A_1	A_2	A_u	B_2	B_2	A_1	B_1	B_u	A_u	B_u
B_{2u}	A_2	A_1	A_2	A_1	A_u	B_3	B_1	B_2	A_1	B_u	B_u	A_u
E_{1u}	E	E	E	E	E_u	B_2+B_3	B_1+B_2	A_1+B_2	A_1+B_1	$2B_u$	A_u+B_u	A_u+B_u
E_{2u}	E	E	E	E	E_u	$A+B_1$	A_1+A_2	A_2+B_1	A_2+B_2	$2A_u$	A_u+B_u	A_u+B_u

D_{6h}	C_3	C_2 C_2	C_2' C_2	C_2'' C_2	σ_h C_s	σ_d C_s	σ_d C_s	C_i
A_{1g}	A	A	A	A	A'	A'	A'	A_g
A_{2g}	A	A	B	B	A'	A"	A"	A_g
B_{1g}	A	B	A	B	A"	A'	A"	A_g
B_{2g}	A	B	B	A	A"	A"	A'	A_g
E_{1g}	E	2B	A+B	A+B	2A"	A'+A"	A'+A"	$2A_g$
E_{2g}	E	2A	A+B	A+B	2A'	A'+A"	A'+A"	$2A_g$
A_{1u}	A	A	A	A	A"	A"	A"	A_u
A_{2u}	A	A	B	B	A"	A'	A'	A_u
B_{1u}	A	B	A	B	A'	A"	A'	A_u
B_{2u}	A	B	B	A	A'	A'	A"	A_u
E_{1u}	E	2B	A+B	A+B	2A'	A'+A"	A'+A"	$2A_u$
E_{2u}	E	2A	A+B	A+B	2A"	A'+A"	A'+A"	$2A_u$

C_{6v}	C_6	σ_v C_{3v}	σ_d C_{3v}	$\sigma_v \to \sigma(zx)$ C_{2v}	C_3	C_2	σ_v C_s	σ_d C_s
A_1	A	A_1	A_1	A_1	A	A	A'	A'
A_2	A	A_2	A_2	A_2	A	A	A"	A"
B_1	B	A_1	A_2	B_1	A	B	A'	A"
B_2	B	A_2	A_1	B_2	A	B	A"	A'
E_1	E_1	E	E	B_1+B_2	E	2B	A'+A"	A'+A"
E_2	E_2	E	E	A_1+A_2	E	2A	A'+A"	A'+A"

S_6	C_3	C_i	C_1
A_g	A	A_g	A
E_g	E	$2A^*_g$	2A*
A_u	A	A_u	A
E_u	E	$2A^*_u$	2A*

D_6	C_6	C'_2 D_3	C''_2 D_3	D_2	C_3	C_2 C_2	C'_2 C_2	C''_2 C_2
A_1	A	A_1	A_1	A	A	A	A	A
A_2	A	A_2	A_2	B_1	A	A	B	B
B_1	B	A_1	A_2	B_2	A	B	A	B
B_2	B	A_2	A_1	B_3	A	B	B	A
E_1	E_1	E	E	B_2+B_3	E	2B	A+B	A+B
E_2	E_2	E	E	$A+B_1$	E	2A	A+B	A+B

S_8	C_4	C_2	C_1
A	A	A	A
B	A	A	A
E_1	E	2B*	2A*
E_2	2B*	2A*	2A*
E_3	E	2B*	2A*

D_{6d}	D_6	C_{6v}	C_6	D_{2d}	D_3	C_{3v}	D_2	C_{2v}	S_4	C_3	C_2 C_2	C'_2 C_2	C_s
A_1	A_1	A_1	A	A_1	A_1	A_1	A	A_1	A	A	A	A	A'
A_2	A_2	A_2	A	A_2	A_2	A_2	B_1	A_2	A	A	A	B	A"
B_1	A_1	A_2	A	B_1	A_1	A_2	A	A_2	B	A	A	A	A"
B_2	A_2	A_1	A	B_2	A_2	A_1	B_1	A_1	B	A	A	B	A'
E_1	E_1	E_1	E_1	E	E	E	B_2+B_3	B_1+B_2	E	E	2B	A+B	A'+A"
E_2	E_2	E_2	E_2	B_1+B_2	E	E	$A+B_1$	A_1+B_2	2B	E	2B	A+B	A'+A"
E_3	B_1+B_2	B_1+B_2	2B	E	A_1+A_2	A_1+A_2	B_2+B_3	B_1+B_2	E	2A	2B	A+B	A'+A"
E_4	E_2	E_2	E_2	A_1+A_2	E	E	$A+B_1$	A_1+A_2	2A	E	2A	A+B	A'+A"
E_5	E_1	E_1	E_1	E	E	E	B_2+B_3	B_1+B_2	E	E	2B	A+B	A'+A"

D_{6h}	D_6	C'_2 D_{3h}	C''_2 D_{3h}	C_{6v}	C_{6h}	C'_2 D_{3d}	C''_2 D_{3d}	D_{2h}	C_6	C_{3h}
A_{1g}	A_1	A'_1	A'_1	A_1	A_g	A_{1g}	A_{1g}	A_g	A	A'
A_{2g}	A_2	A'_2	A'_2	A_2	A_g	A_{2g}	A_{2g}	B_{1g}	A	A'
B_{1g}	B_1	A''_1	A''_2	B_2	B_g	A_{1g}	A_{2g}	B_{2g}	B	A"
B_{2g}	B_2	A''_2	A''_1	B_1	B_g	A_{2g}	A_{1g}	B_{3g}	A	A"
E_{1g}	E_1	E"	E"	E_1	E_{1g}	E_g	E_g	$B_{2g}+B_{3g}$	E_1	E"
E_{2g}	E_2	E'	E'	E_2	E_{2g}	E_g	E_g	A_g+B_{1g}	E_2	E'
A_{1u}	A_1	A''_1	A''_1	A_2	A_u	A_{1u}	A_{1u}	A_u	A	A"
A_{2u}	A_2	A''_2	A''_2	A_1	A_u	A_{2u}	A_{2u}	B_{1u}	A	A"
E_{1u}										

$C_{\infty v}$	C_{6v}	C_{4v}	C_{3v}	C_{2v}
A_1	A_1	A_1	A_1	A_1
A_2	A_2	A_2	A_2	A_2
E_1	E_1	E	E	B_1+B_2
E_2	E_2	B_1+B_2	E	A_1+A_2
E_3	B_1+B_2	E	A_1+A_2	B_1+B_2
E_4	E_2	A_1+A_2	E	A_1+A_2
...				

T	D_2	C_3	C_2	C_1
A	A	A	A	A
E	$2A^*$	E	$2A^*$	$2A^*$
F	$B_1+B_2+B_3$	$A+E‡$	$A+2B$	$3A$

$D_{\infty h}$	D_{6h}	C_{6v}	C_{3v}	D_{4h}	C_{4v}	C_{2v}	$C_{\ v}$
Σ_g^+	A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1
Σ_g^-	A_{2g}	A_2	A_2	A_{2g}	A_2	A_2	A_2
Π_g	E_{1g}	E_1	E	E_g	E	B_1+B_2	E_1
Δ_g	E_{2g}	E_2	E	$B_{1g}+B_{2g}$	B_1+B_2	A_1+A_2	E_2
...							
Σ_u^+	A_{2u}	A_1	A_1	A_{2u}	A_1	A_1	A_1
Σ_u^-	A_{1u}	A_2	A_2	A_{1u}	A_2	A_2	A_2
Π_u	E_{1u}	E_1	E	E_u	E	B_1+B_2	E_1
Δ_u	E_{2u}	E_2	E	$B_{1u}+B_{2u}$	B_1+B_2	A_1+A_2	E_2
...							

T_d	T	D_{2d}	C_{3v}	S_4	D_2	C_{2v}	C_3	C_2	C_s
A_1	A	A_1	A_1	A	A	A_1	A	A	A'
A_2	A	B_1	A_2	B	A	A_2	A	A	A''
E	E	A_1+B_1	E	$A+B$	$2A$	A_1+A_2	E	$2A$	$A'+A''$
F_1	F	A_2+E	A_2+E	$A+E$	$B_1+B_2+B_3$	$A_2+B_1+B_2$	$A+E$	$A+2B$	$A'+2A''$
F_2	F	B_2+E	A_1+E	$B+E$	$B_1+B_2+B_3$	$A_1+B_1+B_2$	$A+E$	$A+2B$	$2A'+A''$

T_h	T	D_{2h}	S_6	D_2	C_{2v}	C_{2h}	C_3	C_2	C_s	C_i	C_1
A_g	A	A_g	A_g	A	A_1	A_g	A	A	A'	A_g	A
E_g	E	$2A_g^*$	E_g	$2A^*$	$2A_1^*$	$2A_g^*$	E	$2A^*$	$2A'^*$	$2A_g^*$	$2A^*$
F_g	F	$B_{1g}+B_{2g}+B_{3g}$	$A_g+E_g‡$	$B_1+B_2+B_3$	$A_2+B_1+B_2$	$A+2B_g$	$A+E‡$	$A+2B$	$2A''+A'$	$3A_g$	$3A$
A_u	A	A_u	A_u	A	A_2	A_u	A	A	A''	A_u	A
E_u	E	$2A_u^*$	E_U	$2A^*$	$2A_2^*$	$2A_u^*$	E	$2A^*$	$2A''^*$	$2A_u$	$2A^*$
F_u	F	$B_{1u}+B_{2u}+B_{3u}$	$A_u+E_u‡$	$B_1+B_2+B_3$	$A_1+B_1+B_2$	A_u+2B_u	$A+E‡$	$A+2B$	$2A'+A''$	$3A_u$	$3A$

											C_2, σ_d	C_2', σ_h			
O_h	O	T_d	T_h	T	D_{3d}	D_{4h}	C_{3v}	D_3	S_6	C_3	D_{2d}	D_{2d}	C_{4v}	D_4	C_{4h}
A_{1g}	A_1	A_1	A_g	A	A_{1g}	A_{1g}	A_1	A_1	A_g	A	A_1	A_1	A_1	A_1	A_g
A_{2g}	A_2	A_2	A_g	A	A_{2g}	B_{1g}	A_2	A_2	A_g	A	B_1	B_2	B_1	B_1	B_g
E_g	E	E	E_g	E	E_g	$A_{1g}+B_{1g}$	E	E	E_g	E	A_1+B_1	A_1+B_2	A_1+B_1	A_1+B_1	A_g+B_g
F_{1g}	F_1	F_1	F_g	F	$A_{2g}+E_g$	$A_{2g}+E_g$	A_2+E	A_2+E	A_g+E_g	$A+E$	A_2+E	A_2+E	A_2+E	A_2+E	A_g+E_g
F_{2g}	F_2	F_2	F_g	F	$A_{1g}+E_g$	$B_{2g}+E_g$	A_1+E	A_1+E	A_g+E_g	$A+E$	B_2+E	B_1+E	B_2+E	B_2+E	B_g+E_g
A_{1u}	A_1	A_2	A_u	A	A_{1u}	A_{1u}	A_2	A_1	A_u	A	B_1	B_1	A_2	A_1	A_u
A_{2u}	A_2	A_1	A_u	A	A_{2u}	B_{1u}	A_1	A_2	A_u	A	A_1	A_2	B_2	B_1	B_u
E_u	E	E	E_u	E	E_u	$A_{1u}+B_{1u}$	E	E	E_u	E	A_1+B_1	A_2+B_1	A_2+B_2	A_1+B_1	A_u+B_u
F_{1u}	F_1	F_2	F_u	F	$A_{2u}+E_u$	$A_{2u}+E_u$	A_1+E	A_2+E	A_u+E_u	$A+E$	B_2+E	B_2+E	A_1+E	A_2+E	A_u+E_u
F_{2u}	F_2	F_1	F_u	F	$A_{1u}+E_u$	$B_{2u}+E_u$	A_2+E	A_1+E	A_u+E_u	$A+E$	A_2+E	A_1+E	B_1+E	B_2+E	B_u+E_u

			$3C_2$	$C_2, 2C_2'$	C_2, σ_h	C_2, σ_d	C_2', σ_h	$3C_2$	$C_2, 2C_2'$
O_h	S_4	C_4	D_{2h}	D_{2h}	C_{2v}	C_{2v}	C_{2v}	D_2	D_2
A_{1g}	A	A	A_g	A_g	A_1	A_1	A_1	A	A
A_{2g}	B	B	A_g	B_{1g}	A_1	A_2	B_1	A	B_1
E_g	$A+B$	$A+B$	$2A_g$	A_g+B_{1g}	$2A_1$	A_1+A_2	A_1+B_1	$2A$	$A+B_1$
F_{1g}	$A+E$	$A+E$	$B_{1g}+B_{2g}+B_{3g}$	$B_{1g}+B_{2g}+B_{3g}$	$A_2+B_1+B_2$	$A_2+B_1+B_2$	$A_2+B_1+B_2$	$B_1+B_2+B_3$	$B_1+B_2+B_3$
F_{2g}	$B+E$	$B+E$	$B_{1g}+B_{2g}+B_{3g}$	$A_{1g}+B_{2g}+B_{3g}$	$A_2+B_1+B_2$	$A_1+B_1+B_2$	$A_1+A_2+B_2$	$B_1+B_2+B_3$	$A+B_2+B_3$
A_{1u}	B	A	A_u	A_u	A_2	A_2	A_2	A	A
A_{2u}	A	B	A_u	B_{2u}	A_2	A_1	B_2	A	B1
E_u	$A+B$	$A+B$	$2A_u$	A_u+B_{1u}	$2A_2$	A_1+A_2	A_2+B_2	$2A$	$A+B_1$
F_{1u}	$B+E$	$B+E$	$B_{1u}+B_{2u}+B_{3u}$	$B_{1u}+B_{2u}+B_{3u}$	$A_1+B_1+B_2$	$A_1+B_1+B_2$	$A_1+B_1+B_2$	$B_1+B_2+B_3$	$B_1+B_2+B_3$
[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]

O_h	C_2,σ_h C_{2h}	C_2',σ_h C_{2h}	σ_h C_s	σ_d C_s	C_2 C_2	C_2' C_2	C_i	C_1
A_{1g}	A_g	A_g	A'	A'	A	A	A_g	A
A_{2g}	A_g	B_g	A'	A"	A	B	A_g	A
E_g	$2A_g$	A_g+B_g	2A'	A'+A"	2A	A+B	$2A_g$	2A
F_{1g}	A_g+2B_g	A_g+2B_g	A'+2A"	A'+2A"	A+2B	A+2B	$3A_g$	3A
F_{2g}	A_g+2B_g	$2A_g+B_g$	A'+2A"	2A'+A"	A+2B	2A+B	$3A_g$	3A
A_{1u}	A_u	A_u	A"	A"	A	A	A_u	A
A_{2u}	A_u	B_u	A"	A'	A	B	A_u	A
E_u	$2A_u$	A_u+B_u	2A"	A'+A"	2A	A+B	$2A_u$	2A
F_{1u}	A_u+2B_u	A_u+2B_u	2A'+A"	2A'+A"	A+2B	A+2B	$3A_u$	3A
F_{2u}	A_u+2B_u	$2A_u+B_u$	2A'+A"	A'+2A"	A+2B	2A+B	$3A_u$	3A

I_h	I	C_5	C_3	C_2	C_1
A_g	A	A	A	A	A
A_u	A	A	A	A	A
F_{1g}	F_1	$A+E_1$	A+E	A+2B	3A
F_{1u}	F_1	$A+E_1$	A+E	A+2B	3A
F_{2g}	F_2	$A+E_2$	A+E	A+@B	3A
F_{2u}	F_2	$A+E_2$	A+E	A+2B	3A
G_{1g}	G_1	E_1+E_2	2A+E	2A+2B	4A
G_{1u}	G_1	E_1+E_2	2A+E	2A+2B	4A
H_g	H	$A+E_1+E_2$	A+2E	3A+2B	5A
H_u	H	$A+E_1+E_2$	A+2E	3A+2B	5A

O_h	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	i	$8S_6$	$3o_h$	$6S_4$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		xx+yy+zz
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1		
E_g	2	-1	2	0	0	2	-1	2	0	0		(xx+yy-2zz,xx-
F_{1g}	3	0	-1	1	-1	3	0	-1	1	-1	(R_x,R_y,R_z)	
F_{2g}	3	0	-1	-1	1	3	0	-1	-1	1		(xy,xz,yz)
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1		
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1		
E_u	2	-1	2	0	0	-2	1	-2	0	0		
F_{1u}	3	0	-1	1	-1	-3	0	1	-1	1	(T_x,T_y,T_z)	
F_{2u}	3	0	-1	-1	1	-3	0	1	1	-1		

I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$		
A	1	1	1	1	1		
F_1	3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	(T_x,T_y,T_z); (R_x,R_y,R_z)	xx+yy+zz
F_2	3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1		
G	4	-1	-1	1	0		
H	5	0	0	-1	1		(xx+yy-2zz,xx-yy, xy,xz,yz)

I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	$15\sigma_d$		
A_g	1	1	1	1	1	1	1	1	1	1		xx+yy+zz
A_u	1	1	1	1	1	-1	-1	-1	-1	-1		
F_{1g}	3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	(R_x,R_y,R_z)	
F_{1u}	3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1	-3	$-\frac{1-\sqrt{5}}{2}$	$-\frac{1+\sqrt{5}}{2}$	0	1	(T_x,T_y,T_z)	
F_{2g}	3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	3	$\frac{1+\sqrt{5}}{2}$	$\frac{1-\sqrt{5}}{2}$	0	-1		
F_{2u}	3	$\frac{1-\sqrt{5}}{2}$	$\frac{1+\sqrt{5}}{2}$	0	-1	-3	$-\frac{1+\sqrt{5}}{2}$	$-\frac{1-\sqrt{5}}{2}$	0	1		
G_{1g}	4	-1	-1	1	0	4	-1	-1	-1	0		
G_{1u}	4	-1	-1	1	0	-4	1	1	-1	0		
H_g	5	0	0	-1	1	5	0	0	-1	1		(xx+yy-2zz, xx-yy,xy, xz,yz)
H_u	5	0	0	-1	1	-5	0	0	1	-1		

Appendix C Correlation Tables

C_{2h}	C_2	C_s	C_i
A_g	A	A'	A_g
B_g	B	A"	A_g
A_u	A	A"	A_u
B_u	B	A'	A_u

C_{2v}	C_2	σ(zx) C_s	σ(yz) C_s
A_1	A	A'	A'
A_2	A	A"	A"
B_1	B	A'	A"
B_2	B	A"	A'

D_2	C_2^z	C_2^y	C_2^x
A	A	A	A
B_1	A	B	B
B_2	B	A	B
B_3	B	B	A

D_{2d}	S_4	C_2-C_2^z D_2	C_{2v}	C_2 C_2	C_2' C_2	C_s
A_1	A	A	A_1	A	A	A'
A_2	A	B_1	A_2	A	B	A"
B_1	B	A	A_2	A	B	A"
B_2	B	B_1	A_1	A	B	A'
E	E	B_2+B_3	B_1+B_2	2B	A+B	A'+A"

D_{2h}	D_2	C_2^z C_{2v}	C_2^y C_{2v}	C_2^x C_{2v}	C_2^z C_{2h}	C_2^z C_{2h}	C_2^y C_{2h}	C_2^x C_2	C_2^z C_2	C_2^y C_2	C_2^x C_s	σ_{xy} C_s	σ_{zx} C_s	σ_{yz} C_i
A_g	A	A_1	A_1	A_1	A_g	A_g	A_g	A	A	A	A'	A'	A'	A_g
B_{1g}	B_1	A_2	B_2	B_1	A_g	B_g	B_g	A	B	B	A'	A"	A"	A_g
B_{2g}	B_2	B_1	A_2	B_2	B_g	A_g	B_g	B	A	A	A"	A'	A"	A_g
B_{3g}	B_3	B_2	B_1	A_2	B_g	B_g	A_g	B	B	A	A"	A"	A'	A_g
A_u	A	A_2	A_2	A_2	A_u	A_u	A_u	A	A	A	A"	A"	A"	A_u
B_{1u}	B_1	A_1	B_1	B_2	A_u	B_u	B_u	A	B	B	A"	A'	A'	A_u
B_{2u}	B_2	B_2	A_1	B_1	B_u	A_u	B_u	B	A	B	A'	A"	A'	A_u
B_{3u}	B_3	B_1	B_2	A_1	B_u	B_u	A_u	B	B	A	A'	A'	A"	A_u

C_{3h}	C_3	C_s	C_1
A'	A	A'	A
E'	E	2A'*	2A*
A"	A	A"	A
E"	E	2A"*	2A*

C_{3v}	C_3	C_s
A_1	A	A'
A_2	A	A"
E	E	A'+A"

D_3	C_3	C_2
A_1	A	A
A_2	A	B
E	E	A+B

D_{3d}	D_3	C_{3v}	$S_6=C_{3i}$	C_3	C_{2h}	C_2	C_s	C_i
A_{1g}	A_1	A_1	A_g	A	A_g	A	A'	A_g
A_{2g}	A_2	A_2	A_g	A	B_g	B	A''	A_g
E_g	E	E	E_g	E	A_g+B_g	$A+B$	$A'+A''$	$2A_g$
A_{1u}	A_1	A_2	A_u	A	A_u	A	A''	A_u
A_{2u}	A_2	A_1	A_u	A	B_u	B	A'	A_u
E_u	E	E	E_u	E	A_u+B_u	$A+B$	$A'+A''$	$2A_u$

D_{3h}	C_{3h}	D_3	C_{3v}	$\sigma_h \to \sigma_v(zy)$ C_{2v}	C_3	C_2	σ_h C_s	σ_v C_s
A_1'	A'	A_1	A_1	A_1	A	A	A'	A'
A_2'	A'	A_2	A_2	B_2	A	B	A'	A''
E'	E'	E	E	A_1+B_2	E	$A+B$	$2A'$	$A'+A''$
A_1''	A''	A_1	A_2	A_2	A	A	A''	A''
A_2''	A''	A_2	A_1	B_1	A	B	A''	A'
E''	E''	E	E	A_2+B_1	E	$A+B$	$2A''$	$A'+A''$

C_4	C_2
A	A
B	A
E	$2B$

C_{4h}	C_4	S_4	C_{2h}	C_2	C_s	C_i	C_1
A_g	A	A	A_g	A	A'	A_g	A
B_g	B	B	A_g	A	A'	A_g	A
E_g	E	E	$2B_u^*$	$2B^*$	$2A''^*$	$2A_g^*$	$2A^*$
A_u	A	B	A_u	A	A''	A_u	A
B_u	B	A	A_u	A	A''	A_u	A
E_u	E	E	$2B_u^*$	$2B^*$	$2A'^*$	$2A_u^*$	$2A^*$

C_{4v}	C_4	σ_v C_{2v}	σ_d C_{2v}	C_2	σ_v C_s	σ_d C_s
A_1	A	A_1	A_1	A	A'	A'
A_2	A	A_2	A_2	A	A''	A''
B_1	B	A_1	A_2	A	A'	A''
B_2	B	A_2	A_1	A	A''	A'
E	E	B_1+B_2	B_1+B_2	$2B$	$A'+A''$	$A'+A''$

S_4	C_2	C_1
A	A	A
B	A	A
E	$2B^*$	$2A^*$

D_4	C_2' D_2	C_2'' D_2	C_4	C_2	C_2' C_2	C_2'' C_2
A_1	A	A	A	A	A	A
A_2	B_1	B_1	A	A	B	B
B_1	A	B_1	B	A	A	B
B_2	B_1	A	B	A	B	A
E	B_2+B_3	B_2+B_3	E	$2B$	$A+B$	$A+B$

C_{5v}	C_5	C_s
A_1	A	A'
A_2	A	A''
E_1	E_1	$A'+A''$
E_2	E_2	$A'+A''$

						C_2	C_2'	
D_{4d}	D_4	C_{4v}	S_8	C_4	C_{2v}	C_2	C_2	C_s
A_1	A_1	A_1	A	A	A_1	A	A	A'
A_2	A_2	A_2	A	A	A_2	A	A	A"
B_1	A_1	A_2	B	A	A_1	A	B	A'
B_2	A_2	A_1	B	A	A_1	A	B	A'
E_1	E	E	E_1	E	B_1+B_2	2B	A+B	A'+A"
E_2	B_1+B_2	B_1+B_2	E_2	2B	A_1+A_2	2A	A+B	A'+A"
E_3	E	E	E_3	E	B_1+B_2	2B	A+B	A'+A"

C_{5h}	C_5	C_s	C_1
A'	A	A'	A
E_1'	E_1	2A'*	2A*
E_2'	E_2	2A'*	2A*
A"	A	A"	A
E_1''	A	2A"*	2A*
E_2''	E_2	2A"*	2A*

		C_2'	C_2''			C_2'	C_2''			C_2'	C_2''	C_2,σ_v	C_2,σ_d
D_{4h}	D_4	D_{2d}	D_{2d}	C_{4v}	C_{4h}	D_{2h}	D_{2h}	C_4	S_4	D_2	D_2	C_{2v}	C_{2v}
A_{1g}	A_1	A_1	A_1	A_1	A_g	A_g	A_g	A	A	A	A	A_1	A_1
A_{2g}	A_2	A_2	A_2	A_2	A_g	B_{1g}	B_{1g}	A	A	B_1	B_1	A_2	A_2
B_{1g}	B_1	B_1	B_2	B_1	B_g	A_g	B_{1g}	B	B	A	B_1	A_1	A_2
B_{2g}	B_2	B_2	B_1	B_2	B_g	B_{1g}	A_g	B	B	B_1	A	A_2	A_1
E_g	E	E	E	E	E_g	$B_{2g}+B_{3g}$	$B_{2g}+B_{3g}$	E	E	B_2+B_3	B_2+B_3	B_1+B_2	B_1+B_2
A_{1u}	A_1	B_1	B_1	A_2	A_u	A_u	A_u	A	B	A	A	A_2	A_2
A_{2u}	A_2	B_2	B_2	A_1	A_u	B_{1u}	B_{1u}	A	B	B_1	B_1	A_1	A_1
B_{1u}	B_1	A_1	A_2	B_2	B_u	A_u	B_{1u}	B	A	A	B_1	A_2	A_1
B_{2u}	B_2	A_2	A_1	B_1	B_u	B_{1u}	A_u	B	A	B_1	A	A_1	A_2
E_u	E	E	E	E	E_u	$B_{2u}+B_{3u}$	$B_{2u}+B_{3u}$	E	E	B_2+B_3	B_2+B_3	B_1+B_2	B_1+B_2

	C_2'	C_2''	C_2	C_2'	C_2''	C_2	C_2'	C_2''	σ_h	σ_v	σ_d	
D_{4h}	C_{2v}	C_{2v}	C_{2h}	C_{2h}	C_{2h}	C_2	C_2	C_2	C_s	C_s	C_s	C_i
A_{1g}	A_1	A_1	A_g	A_g	A_g	A	A	A	A'	A'	A'	A_g
A_{2g}	B_2	B_2	A_g	B_g	B_g	A	B	A	A'	A"	A"	A_g
B_{1g}	A_1	B_2	A_g	A_g	B_g	A	A	B	A'	A'	A"	A_g
B_{2g}	B_2	A_1	A_g	B_g	A_g	A	B	A	A'	A"	A'	A_g
E_g	A_2+B_1	A_2+B_1	$2B_g$	A_g+B_g	A_g+B_g	2B	A+B	A+B	2A"	A'+A"	A'+A"	$2A_g$
A_{1u}	A_2	A_2	A_u	A_u	A_u	A	A	A	A"	A"	A"	A_u
A_{2u}	B_1	B_1	A_u	B_u	B_u	A	B	B	A"	A'	A'	A_u
B_{1u}	A_2	B_1	A_u	A_u	B_u	A	A	B	A"	A"	A'	A_u
B_{2u}	B_1	A_2	A_u	B_u	A_u	A	B	A	A"	A'	A"	A_u
E_u	A_1+B_2	A_1+B_2	$2B_u$	A_u+B_u	A_u+B_u	2B	A+B	A+B	2A'	A'+A"	A'+A"	$2A_u$

D_{5d}	D_5	C_{5v}	C_5	C_2	C_s	C_i
A_{1g}	A_1	A_1	A	A	A'	A_g
A_{2g}	A_2	A_2	A	A	A''	A_g
E_{1g}	E_1	E_1	E_1	$A+B$	$A'+A''$	$2A_g$
E_{2g}	E_2	E_2	E_2	$A+B$	$A'+A''$	$2A_g$
A_{1u}	A_1	A_2	A	A	A''	A_u
A_{2u}	A_2	A_1	A	B	A'	A_u
E_{1u}	E_1	E_1	E_1	$A+B$	$A'+A''$	$2A_u$
E_{2u}	E_2	E_2	E_2	$A+B$	$A'+A''$	$2A_u$

D_5	C_5	C_2
A_1	A	A
A_2	A	B
E_1	E_1	$A+B$
E_2	E_2	$A+B$

					$\sigma_h \to \sigma(zx)$		σ_h	σ_v
D_{5h}	D_5	C_{5v}	C_{5h}	C_5	C_{2v}	C_2	C_s	C_s
A_1'	A_1	A_1	A'	A	A_1	A	A'	A'
A_2'	A_2	A_2	A'	A	B_1	B	A'	A''
E_1'	E_1	E_1	E_1'	E_1	A_1+B_2	$A+B$	$2A'$	$A'+A''$
E_2'	E_2	E_2	E_2'	E_2	A_1+B_2	$A+B$	$2A'$	$A'+A''$
A_1''	A_1	A_2	A''	A	A_2	A	A''	A''
A_2''	A_2	A_1	A''	A''	B_2	B	A''	A'
E_1''	E_1	E_1	E_1''	E_1	A_2+B_2	$A+B$	$2A''$	$A'+A''$
E_2''	E_2	E_2	E_2''	E_2	A_2+B_2	$A+B$	$2A''$	$A'+A''$

C_6	C_3	C_2	C_1
A	A	A	A
B	A	B	A
E_1	E	$2B^*$	$2A^*$
E_2	E	$2A^*$	$2A^*$

C_{6h}	C_6	C_{3h}	S_6	C_{2h}	C_3	C_2	C_s	C_i	C_1
A_g	A	A'	A_g	A_g	A	A	A'	A_g	A
B_g	B	A''	A_g	B_g	A	B	A''	A_g	A
E_{1g}	E_1	E''	E_g	$2B_g^*$	E	$2B^*$	$2A''^*$	$2A_g^*$	$2A^*$
E_{2g}	E_2	E'	E_g	$2A_g^*$	E	$2A^*$	$2A'^*$	$2A_g^*$	$2A^*$
A_u	A	A''	A_u	A_u	A	A	A''	A_u	A
B_u	B	A'	A_u	B_u	A	B	A'	A_u	A
E_{1u}	E_1	E'	E_u	$2B_u^*$	E	$2B^*$	$2A'^*$	$2A_u^*$	$2A^*$
E_{2u}	E_2	E''	E_u	$2A_u^*$	E	$2A^*$	$2A''^*$	$2A_u^*$	$2A^*$

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