

C. GROUP THEORY IN SPECTROSCOPY

Quite a lot of what we will be talking about in this Appendix was invented by Evariste Galois. He was only 21 when he died in a duel (*cherchez la femme!*). Galois spent his last night writing down his group theory.

Evariste Galois (1811–1832), French mathematician, also created many fundamental ideas in the theory of algebraic equations.



The group theory in this textbook will be treated in a practical way, as one of useful tools.¹

Our goal will be to predict the selection rules in ultraviolet (UV), visual (VIS) and infrared (IR) molecular spectra.

We will try to be concise, but examples need explanations, there are few lovers of dry formulae.

1 GROUP

Imagine a set of elements \hat{R}_i , $i = 1, 2, \dots, g$. We say that they form a group G of order² g , if the following four conditions are satisfied:

1. An operation exists called “multiplication”, $\hat{R}_i \cdot \hat{R}_j$, which associates every pair of the elements of G with another element of G , i.e. $\hat{R}_i \cdot \hat{R}_j = \hat{R}_k$. Hereafter

¹ Rather than as a field of abstract mathematics. Symmetry may be viewed either as something beautiful or primitive. It seems that, from the psychological point of view, symmetry stresses people’s longing for simplicity, order and understanding. On the other hand, symmetry means less information and hence often a kind of wearingly dull stimuli. Possibly the interplay between these two opposite features leads us to consider *broken* symmetry as beautiful. Happily enough, trees and leaves exhibit broken symmetry and look beautiful. Ancient architects knew the secrets of creating beautiful buildings, which relied on breaking symmetry, in a substantial way, but almost invisible from a distance.

² g may be finite or infinite. In most applications of the present Appendix, g will be finite.

- the multiplication $\hat{R}_i \cdot \hat{R}_j$ will be denoted simply as $\hat{R}_i \hat{R}_j$. Thus the elements can multiply each other and the result always belongs to the group.
2. The multiplication is associative,³ i.e. for any three elements of G we have $\hat{R}_i(\hat{R}_j \hat{R}_k) = (\hat{R}_i \hat{R}_j) \hat{R}_k$.
 3. Among $\hat{R}_i \in G$ an *identity* element exists, denoted by \hat{E} , with a nice property: $\hat{R}_i \hat{E} = \hat{R}_i$ and $\hat{E} \hat{R}_i = \hat{R}_i$ for any i .
 4. For each \hat{R}_i we can find an element of G (denoted as \hat{R}_i^{-1} , called the *inverse* element with respect to \hat{R}_i), such that $\hat{R}_i \hat{R}_i^{-1} = \hat{E}$, also $\hat{R}_i^{-1} \hat{R}_i = \hat{E}$.

Example 1. A four-element group. The elements 1, -1 , i , $-i$ with the chosen operation the ordinary multiplication of numbers, form a group of order 4. Indeed, any product of these numbers gives one of them. Here is the corresponding “multiplication table”

		second in the product			
		1	-1	i	$-i$
first in the product	1	1	-1	i	$-i$
	-1	-1	1	$-i$	i
	i	i	$-i$	-1	1
	$-i$	$-i$	i	1	-1

Note that

ABELIAN GROUP:
The table is *symmetric* with respect to the diagonal. A group with a symmetric multiplication table is called Abelian.

Abelian group

The associativity requirement is of course satisfied. The unit element is 1. You can always find an inverse element. Indeed, for 1 it is 1, for -1 it is -1 , for i it is $-i$, for $-i$ it is i . Thus, all conditions are fulfilled and $g = 4$.

Example 2. Group of integers. Let us take as G the set of integers with the “multiplication” being the regular addition of numbers. Let us check. The sum of two integers is an integer, so requirement 1 is satisfied. The operation is associative, because addition is. The unit element is, of course, 0. The inverse element to an integer means the opposite number. Thus, G is a group of order $g = \infty$.

Example 3. Group of non-singular matrices. All non-singular $n \times n$ matrices⁴ with matrix multiplication as the operation, form a group. Let us see. Multiplication of a non-singular matrix A (i.e. $\det A \neq 0$) by a non-singular matrix B gives a non-singular matrix $C = AB$, because $\det C = \det A \det B \neq 0$. The unit element is the unit matrix $\mathbf{1}$, the inverse element exists (this is why we needed the non-singularity) and is equal to A^{-1} . Also from the matrix multiplication rule we have $(AB)C = A(BC)$. This is a group of order ∞ .

³Thanks to this, expressions similar to $\hat{R}_i \hat{R}_j \hat{R}_k$ have unambiguous meaning.
⁴See Appendix A.

Example 4. Group of unitary matrices $U(n)$. In particular, all the unitary $n \times n$ matrices form a group with matrix multiplication as the group multiplication operation. Let us check. Any such multiplication is feasible and the product represents a unitary matrix (if matrices U_1 and U_2 are unitary, i.e. $U_1^\dagger = U_1^{-1}$ and $U_2^\dagger = U_2^{-1}$, then $U = U_1 U_2$ is also unitary, because $U^{-1} = U_2^{-1} U_1^{-1} = U_2^\dagger U_1^\dagger = (U_1 U_2)^\dagger = U^\dagger$), matrix multiplication is associative, the identity element means the $n \times n$ unit matrix, and the inverse matrix $U^{-1} = U^\dagger \equiv (U^T)^*$ always exists. In physics this group is called $U(n)$.

Example 5. $SU(n)$ group. The group (famous in physics) $SU(n)$ for $n \geq 2$ is defined as the subset of $U(n)$ of such matrices U that $\det U = 1$ with the same multiplication operation. Indeed, since $\det(U_1 U_2) = \det U_1 \det U_2$, then multiplication of any two elements of the $SU(n)$ gives an element of $SU(n)$. Also of great importance in physics is the $SO(n)$ group, that is the $SU(n)$ group with real (i.e. orthogonal) matrices.⁵ SO(3)

Unitary vs symmetry operation

Let us take the $SO(3)$ group of all rotations of the coordinate system in 3D (the *Cartesian 3D Euclidean space*, see Appendix B, p. 895). The rotation operators acting in this space will be denoted by \hat{R} and defined as follows: operator \hat{R} acting on a vector \mathbf{r} produces vector $\hat{R}\mathbf{r}$:

$$\hat{R}\mathbf{r} = \mathbf{R}\mathbf{r}, \quad (\text{C.1})$$

where⁶ \mathbf{R} represents an orthogonal matrix of dimension 3. The orthogonality guarantees that the transformation preserves the vector dot (or scalar) products (and therefore their lengths as well).

Let us take an arbitrary function $f(\mathbf{r})$ of position \mathbf{r} . Now, for each of the operators \hat{R} let us construct the corresponding operator $\hat{\mathcal{R}}$ that *moves the function in space without its deformation*. Generally, we obtain another function, which means that $\hat{\mathcal{R}}$ operates in the Hilbert space. The construction of operator $\hat{\mathcal{R}}$ is based on the following description

$$\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r}). \quad (\text{C.2})$$

⁵Recall (Appendix A) that for a unitary matrix U we have $\det U = \exp(i\phi)$. For orthogonal matrices (i.e. unitary ones with all the elements real) $\det U = \pm 1$. This does not mean that the $SU(n)$ is composed of the orthogonal matrices only. For example, all four 2×2 matrices:

$$\begin{Bmatrix} 1 & 0 \\ 0 & 1 \end{Bmatrix}, \begin{Bmatrix} -1 & 0 \\ 0 & -1 \end{Bmatrix}, \begin{Bmatrix} 0 & i \\ i & 0 \end{Bmatrix}, \begin{Bmatrix} 0 & -i \\ -i & 0 \end{Bmatrix}$$

have determinants equal to 1 and belong to $SU(2)$, while only the first two belong to $SO(2)$.

⁶The point in 3D space is indicated by vector $\mathbf{r} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}$.

This means that the displacement in space of function $f(\mathbf{r})$ is simply equivalent to leaving the function intact, but instead *inverting the displacement of the coordinate system*.⁷

Operators $\hat{\mathcal{R}}$ rotate functions without their deformation, therefore they preserve the scalar products in the Hilbert space and are unitary. They form a group isomorphic with the group of operators \hat{R} , because they have the same multiplication table as operators \hat{R} : if $\hat{R} = \hat{R}_1 \hat{R}_2$, then $\hat{\mathcal{R}} = \hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2$, where $\hat{\mathcal{R}}_1 f(\mathbf{r}) = f(\hat{R}_1^{-1} \mathbf{r})$ and $\hat{\mathcal{R}}_2 f(\mathbf{r}) = f(\hat{R}_2^{-1} \mathbf{r})$. Indeed,⁸ $\hat{\mathcal{R}} f = (\hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2) f(\mathbf{r}) = f(\hat{R}_2^{-1} \hat{R}_1^{-1} \mathbf{r}) = f(\hat{R}^{-1} \mathbf{r})$.

UNITARY VS SYMMETRY OPERATION

A unitary operation is a symmetry operation of function $f(\mathbf{r})$, when $\hat{\mathcal{R}} f(\mathbf{r}) = f(\mathbf{r})$.

Example 6. Rotation of a point. Operator $\hat{R}(\alpha; z)$ of the rotation of a point with coordinates x, y, z by angle α about axis z gives a point with coordinates x', y', z' (Fig. C.1.a)

$$\begin{aligned} x' &= r \cos(\phi + \alpha) = r \cos \phi \cos \alpha - r \sin \phi \sin \alpha = x \cos \alpha - y \sin \alpha, \\ y' &= r \sin(\phi + \alpha) = r \sin \phi \cos \alpha + r \cos \phi \sin \alpha = x \sin \alpha + y \cos \alpha, \\ z' &= z, \end{aligned}$$

the corresponding transformation matrix of the old to the new coordinates, therefore, is

$$U = \begin{bmatrix} \cos \alpha & -\sin \alpha & 0 \\ \sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We obtain the same new coordinates if the point remains still while the coordinate system rotates in the opposite direction (i.e. by angle $-\alpha$).

Example 7. Rotation of an atomic orbital. Let us construct a single spherically symmetric Gaussian orbital $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_0|^2]$ in Hilbert space for one electron. Let the atomic orbital be centred on the point indicated by vector \mathbf{r}_0 . Operator $\hat{\mathcal{R}}(\alpha; z)$ has to perform the rotation of a *function*⁹ by angle α about axis z

⁷Motion is relative. Let us concentrate on a rotation by angle α . The result is the same if:

- the coordinate system stays still, but the point rotates by angle α
- or, the point does not move, while the coordinate system rotates by angle $-\alpha$.

What would happen if function $f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ is rotated? Then we will do the following: $\hat{\mathcal{R}} f(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) = f(\hat{R}^{-1} \mathbf{r}_1, \hat{R}^{-1} \mathbf{r}_2, \dots, \hat{R}^{-1} \mathbf{r}_N)$.

⁸This result is correct, but the routine notation works in a quite misleading way here when suggesting that $(\hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2) f(\mathbf{r})$ and $f(\hat{R}_1^{-1} \hat{R}_2^{-1} \mathbf{r})$ mean the same. However, we derive the correct result in the following way. First, from the definition we have $\hat{\mathcal{R}}_2 f(\mathbf{r}) = (R_2^{-1} \mathbf{r}) \equiv g_2(\mathbf{r})$. Then we get $(\hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2) f(\mathbf{r}) = \hat{\mathcal{R}}_1 [\hat{\mathcal{R}}_2 f(\mathbf{r})] = \hat{\mathcal{R}}_1 g_2(\mathbf{r}) = g_2(R_1^{-1} \mathbf{r}) = \hat{\mathcal{R}}_2 f(R_1^{-1} \mathbf{r}) = f(R_2^{-1} R_1^{-1} \mathbf{r})$.

⁹This orbital represents our *object* rotating by α . The coordinate system remains unchanged while the object moves. The job will be done by operator $\hat{\mathcal{R}}(\alpha; z)$.

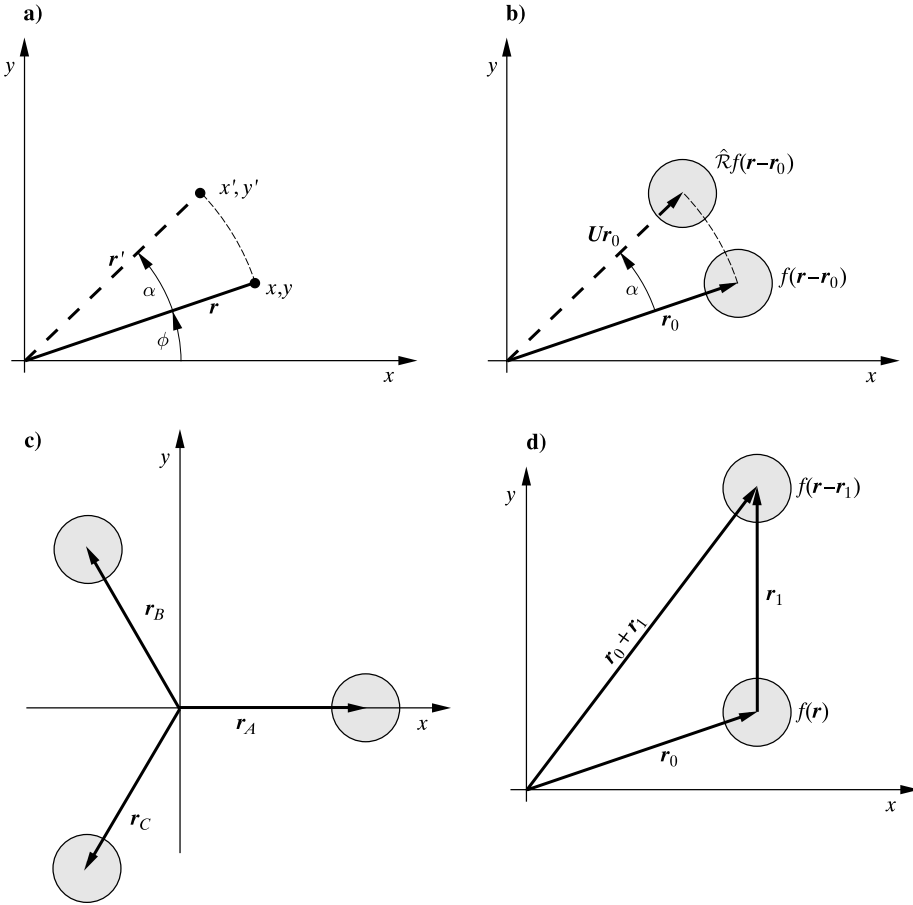


Fig. C.1. Examples of an isometric operation. (a) Unitary operation: rotation of a point by angle α about axis z . The old position of the point is indicated by the vector \mathbf{r} , the new position by \mathbf{r}' (of the same length). (b) Unitary operation: rotation of function $f(\mathbf{r} - \mathbf{r}_0)$ by angle α about axis z . As a result we have function $f(\mathbf{r} - U\mathbf{r}_0)$, which in general represents a function which differs from $f(\mathbf{r} - \mathbf{r}_0)$. (c) The unitary operation which represents a symmetry operation: rotation by angle $\alpha = 120^\circ$ of function $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_A|^2] + \exp[-|\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \mathbf{r}_C|^2]$, where vectors $\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_C$ are of the same length and form a “Mercedes trademark” (angle 120°). The new function is identical to the old one. (d) Translational operator by vector \mathbf{r}_1 : $\hat{\mathcal{R}}(\mathbf{r}_1)$ applied to the Gaussian function $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_0|^2]$ gives $\hat{\mathcal{R}}(\mathbf{r}_1)f(\mathbf{r}) = f(\hat{\mathcal{R}}^{-1}\mathbf{r}) = \exp[-|\hat{\mathcal{R}}^{-1}\mathbf{r} - \mathbf{r}_0|^2] = \exp[-|\mathbf{r} - \mathbf{r}_1 - \mathbf{r}_0|^2] = \exp[-|\mathbf{r} - (\mathbf{r}_1 + \mathbf{r}_0)|^2] = f(\mathbf{r} - \mathbf{r}_1)$, i.e. the function is shifted in space by vector \mathbf{r}_1 with respect to the original function.

(Fig. C.1.b), which corresponds to a rotation in Hilbert space.¹⁰ According to the definition of a rotation, what we need is $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{\mathcal{R}}^{-1}\mathbf{r})$. Since operator $\hat{\mathcal{R}}$ corresponds to matrix U , then $\hat{\mathcal{R}}^{-1}$ corresponds to U^{-1} . The last matrix is simply

¹⁰We will obtain another (because differently centred) function.

$$U^{-1} = U^T = \begin{bmatrix} \cos \alpha & \sin \alpha & 0 \\ -\sin \alpha & \cos \alpha & 0 \\ 0 & 0 & 1 \end{bmatrix}.$$

We obtain the following chain of transformations

$$\begin{aligned} f(\hat{R}^{-1}\mathbf{r}) &= \exp[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_0|^2] = \exp[-|\hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0|^2] \\ &= \exp[-\langle \hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0 | \hat{R}^{-1}\mathbf{r} - \hat{R}^{-1}\hat{R}\mathbf{r}_0 \rangle] \\ &= \exp[-\langle \hat{R}\hat{R}^{-1}\mathbf{r} - \hat{R}\hat{R}^{-1}\hat{R}\mathbf{r}_0 | \mathbf{r} - \hat{R}\mathbf{r}_0 \rangle] \\ &= \exp[-\langle \mathbf{r} - \hat{R}\mathbf{r}_0 | \mathbf{r} - \hat{R}\mathbf{r}_0 \rangle] = \exp[-|\mathbf{r} - \hat{R}\mathbf{r}_0|^2]. \end{aligned}$$

Thus, the centre of the orbital undergoes rotation and therefore $\hat{\mathcal{R}}f(\mathbf{r})$ indeed represents the spherically symmetric orbital¹¹ displaced by angle α .

Since *in general* for any value of angle α function $\exp[-|\mathbf{r} - \mathbf{U}\mathbf{r}_0|^2]$ is not equal to $\exp[-|\mathbf{r} - \mathbf{r}_0|^2]$, unitary operation $\hat{\mathcal{R}}$ is *not* a symmetry operation on the object.

If, however, $\alpha = 2\pi n$, $n = 0, \pm 1, \pm 2, \dots$, then $\hat{\mathcal{R}}f(\mathbf{r}) = f(\mathbf{r})$ and $\hat{\mathcal{R}}(2\pi n; z)$ is¹² a symmetry operation.

Example 8. Rotation of a particular sum of atomic orbitals. Let us take the example of the *sum* of three spherically symmetric Gaussian orbitals:

$$f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_A|^2] + \exp[-|\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \mathbf{r}_C|^2],$$

where vectors $\mathbf{r}_A, \mathbf{r}_B, \mathbf{r}_C$ are of the same length and form the “Mercedes sign” (angles equal to 120°), Fig. C.1.c. Let us take operator $\hat{\mathcal{R}}(\alpha = 120^\circ; z)$ corresponding to matrix U . Application of $\hat{\mathcal{R}}$ to function $f(\mathbf{r})$ is equivalent to¹³

$$\begin{aligned} f(\hat{R}^{-1}\mathbf{r}) &= \exp[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_A|^2] + \exp[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_C|^2] \\ &= \exp[-|\mathbf{r} - \hat{R}\mathbf{r}_A|^2] + \exp[-|\mathbf{r} - \hat{R}\mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \hat{R}\mathbf{r}_C|^2]. \end{aligned}$$

¹¹The definition $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$ can transform anything: from the spherically symmetric Gaussian orbital through a molecular orbital (please recall it can be represented by the LCAO expansion) to the Statue of Liberty. Indeed, do you want to rotate the Statue of Liberty? Then leave the Statue in peace, but transform (in the opposite way) your Cartesian coordinate system.

More general transformations, allowing deformation of objects, could also be described by this formula $\hat{\mathcal{R}}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$, but operator \hat{R} would be non-unitary.

¹²The transformed and non-transformed orbitals coincide.

¹³We use the result from the last example.

From the figure (or from the matrix) we have $\hat{R}\mathbf{r}_A = \mathbf{r}_B$; $\hat{R}\mathbf{r}_B = \mathbf{r}_C$; $\hat{R}\mathbf{r}_C = \mathbf{r}_A$. This gives

$$\hat{R}f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_B|^2] + \exp[-|\mathbf{r} - \mathbf{r}_C|^2] + \exp[-|\mathbf{r} - \mathbf{r}_A|^2] = f(\mathbf{r}).$$

We have obtained our old function. $\hat{R}(\alpha = 120^\circ; z)$ is therefore the *symmetry operation*¹⁴ $f(\mathbf{r})$.

$\hat{R}(\alpha = 120^\circ; z)$ represents a symmetry operation not only for function f , but also for other objects which have the *symmetry of an equilateral triangle*.

Example 9. Rotation of a many-electron wave function. If, in the last example, we had taken a three-electronic function as the *product* of the Gaussian orbitals

$$f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \exp[-|\mathbf{r}_1 - \mathbf{r}_A|^2] \cdot \exp[-|\mathbf{r}_2 - \mathbf{r}_B|^2] \cdot \exp[-|\mathbf{r}_3 - \mathbf{r}_C|^2],$$

then after applying $\hat{R}(\alpha = 120^\circ; z)$ to f we would obtain, using an almost identical procedure,

$$\begin{aligned} \hat{R}f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &= f(\hat{R}^{-1}\mathbf{r}_1, \hat{R}^{-1}\mathbf{r}_2, \hat{R}^{-1}\mathbf{r}_3) \\ &= \exp[-|\mathbf{r}_1 - \mathbf{r}_B|^2] \cdot \exp[-|\mathbf{r}_2 - \mathbf{r}_C|^2] \cdot \exp[-|\mathbf{r}_3 - \mathbf{r}_A|^2], \end{aligned}$$

which represents a completely different function than the original $f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$! Thus, \hat{R} does not represent any symmetry operation for $f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$. If, however, we had taken a symmetrized function, e.g., $\tilde{f}(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) = \sum_P \hat{P}f(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)$, where \hat{P} permutes the centres A, B, C, and the summation goes over all permutations, we would obtain an \tilde{f} that would turn out to be symmetric with respect to $\hat{R}(\alpha = 120^\circ; z)$.

Example 10. Translation. Translation cannot be represented as a matrix transformation (C.1). It is, however, an *isometric operation*, i.e. preserves the distances among the points of the transformed object. This is sufficient for us. Let us enlarge the set of the allowed operations in 3D Euclidean space by isometry. Similarly, as in the case of rotations let us define a shift of the *function* $f(\mathbf{r})$. A shift of *function* $f(\mathbf{r})$ by vector \mathbf{r}_1 is such a transformation $\hat{R}(\mathbf{r}_1)$ (in the Hilbert space) that the new function $\tilde{f}(\mathbf{r}) = f(\mathbf{r} - \mathbf{r}_1)$. As an example let us take function $f(\mathbf{r}) = \exp[-|\mathbf{r} - \mathbf{r}_0|^2]$ and let us shift it by vector \mathbf{r}_1 . Translations obey the known relation (C.2):

isometric
operation

$$\begin{aligned} \hat{R}(\mathbf{r}_1)f(\mathbf{r}) &= f(\hat{R}^{-1}\mathbf{r}) = \exp[-|\hat{R}^{-1}\mathbf{r} - \mathbf{r}_0|^2] \\ &= \exp[-|\mathbf{r} - \mathbf{r}_1 - \mathbf{r}_0|^2] = \exp[-|\mathbf{r} - (\mathbf{r}_1 + \mathbf{r}_0)|^2] = f(\mathbf{r} - \mathbf{r}_1). \end{aligned}$$

¹⁴Note that, e.g., if one of the 1s orbitals had the opposite sign, function $f(\mathbf{r})$ would not have the symmetry of an equilateral triangle, although it would also be invariant with respect to *some* of the operations of an equilateral triangle.

Function $f(\mathbf{r})$ had been concentrated around point \mathbf{r}_0 , while the new function $\hat{R}(\mathbf{r}_1)f(\mathbf{r})$ is concentrated around the point indicated by vector $\mathbf{r}_1 + \mathbf{r}_0$, i.e. the function has been shifted by \mathbf{r}_1 (Fig. C.1.d). This transformation is (similar to case of rotations) unitary, because the scalar product between two functions f_1 and f_2 shifted by the same operation is preserved: $\langle f_1(\mathbf{r}) | f_2(\mathbf{r}) \rangle = \langle f_1(\mathbf{r} - \mathbf{r}_1) | f_2(\mathbf{r} - \mathbf{r}_1) \rangle$.

Symmetry group of the ammonia molecule

Imagine a model of the NH_3 molecule (rigid trigonal pyramid), Fig. C.2. A student sitting at the table plays with the model. We look at the model, then close our eyes for a second, and open them again. We see that the student smiles, but the coordinate system, the model and its position with respect to the coordinate system look exactly the same as before. Could the student have changed the position of the model? Yes, it is possible. For example, the student could rotate the model about the z axis (perpendicular to the table) by 120° , he might exchange two NH bonds in the model, he may also do nothing. Whatever the student could do is called a *symmetry operation*.

Let us make a list of all the symmetry operations allowed for the ammonia molecule (Table C.1). To this end, let us label the vertices of the triangle a, b, c and locate it in such a way that the centre of the triangle coincides with the origin of the coordinate system, and the y axis indicates vortex a .

Now let us check whether the operations given in Table C.1 form a group. Four conditions have to be satisfied. The first condition requires the existence of “multiplication” in the group, and that the product of any two elements gives an element of the group: $\hat{R}_i \hat{R}_j = \hat{R}_k$. The elements will be the symmetry operations of the equilateral triangle. The product $\hat{R}_i \hat{R}_j = \hat{R}_k$ means that operation \hat{R}_k gives the same result as applying to the triangle operation \hat{R}_j first, and then the result is

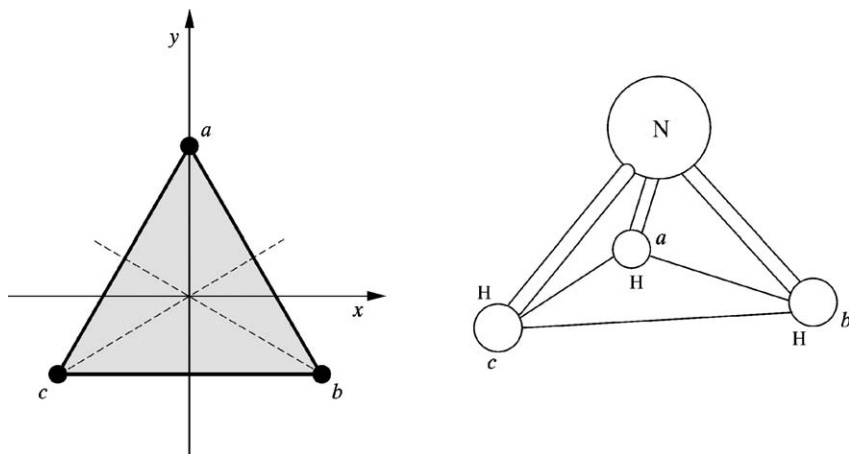


Fig. C.2. The equilateral triangle and the coordinate system. Positions a, b, c are occupied by hydrogen atoms, the nitrogen atom is (symmetrically) above the plane.

Table C.1. Symmetry operations of the ammonia molecule (the reflections pertain to the mirror planes perpendicular to the triangle, Fig. C.2, and go through the centre of the triangle)

Symbol	Description	Symbolic explanation
\hat{E}	do nothing	$\hat{E} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} a \\ c \\ b \end{bmatrix}$
\hat{A}	reflection in the plane going through point a shown in Fig. C.2	$\hat{A} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} a \\ b \\ c \end{bmatrix}$
\hat{B}	reflection in the plane going through point b shown in Fig. C.2	$\hat{B} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} c \\ a \\ b \end{bmatrix}$
\hat{C}	reflection in the plane going through point c shown in Fig. C.2	$\hat{C} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} b \\ c \\ a \end{bmatrix}$
\hat{D}	rotation by 120° (clockwise)	$\hat{D} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} c \\ b \\ a \end{bmatrix}$
\hat{F}	rotation by -120° (counter-clockwise)	$\hat{F} \begin{bmatrix} a \\ c \\ b \end{bmatrix} = \begin{bmatrix} b \\ a \\ c \end{bmatrix}$

subject to operation \hat{R}_i . In this way the “multiplication table” C.2 can be obtained.

Further, using the table we may check whether the operation is associative. For example, we check whether $\hat{A}(\hat{B}\hat{C}) = (\hat{A}\hat{B})\hat{C}$. The left-hand side gives: $\hat{A}(\hat{B}\hat{C}) = \hat{A}\hat{D} = \hat{B}$. The right-hand side is: $(\hat{A}\hat{B})\hat{C} = \hat{D}\hat{C} = \hat{B}$. It agrees. It will agree for all the other entries in the table.

The unit operation is \hat{E} , as seen from the table, because multiplying by \hat{E} does not change anything: $\hat{E}\hat{R}_i = \hat{R}_i\hat{E} = \hat{R}_i$. Also, using the table again, we can find the inverse element to any of the elements. Indeed, $\hat{E}^{-1} = \hat{E}$, because \hat{E} times just \hat{E} equals to \hat{E} . Further, $\hat{A}^{-1} = \hat{A}$, because \hat{A} times \hat{A} equals \hat{E} , etc., $\hat{B}^{-1} = \hat{B}$, $\hat{C}^{-1} = \hat{C}$, $\hat{D}^{-1} = \hat{F}$, $\hat{F}^{-1} = \hat{D}$.

Thus all the requirements are fulfilled and all these operations form a group of order $g = 6$. Note that in this group the operations do not necessarily commute, e.g., $\hat{C}\hat{D} = \hat{A}$, but $\hat{D}\hat{C} = \hat{B}$ (the group is not Abelian).

Table C.2. Group multiplication table

		second in the product					
first in the product	\hat{R}_i	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}
	\hat{E}	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}
	\hat{A}	\hat{A}	\hat{E}	\hat{D}	\hat{F}	\hat{B}	\hat{C}
	\hat{B}	\hat{B}	\hat{F}	\hat{E}	\hat{D}	\hat{C}	\hat{A}
	\hat{C}	\hat{C}	\hat{D}	\hat{F}	\hat{E}	\hat{A}	\hat{B}
	\hat{D}	\hat{D}	\hat{C}	\hat{A}	\hat{B}	\hat{F}	\hat{E}
	\hat{F}	\hat{F}	\hat{B}	\hat{C}	\hat{A}	\hat{E}	\hat{D}

Classes

The group elements can be all divided into disjoint sets called classes. A class (to put it first in a simplified way) represents a set of operations that are similar, e.g., three reflection operations \hat{A} , \hat{B} and \hat{C} constitute one class, the rotations \hat{D} and \hat{F} form the second class, the third class is simply the element \hat{E} . Now, the precise definition.

CLASS

A class is a set of elements that are conjugate one to another. An element \hat{R}_i is conjugate with \hat{R}_j if we can find in group G such an element (let us denote it by \hat{X}) that $\hat{X}^{-1}\hat{R}_j\hat{X} = \hat{R}_i$.

Then, of course, element \hat{R}_j is a conjugate to \hat{R}_i as well. We check this by multiplying \hat{R}_i from the left by $\hat{X} = \hat{Y}^{-1}$, and from the right by $\hat{X}^{-1} = \hat{Y}$ (which yields $\hat{Y}^{-1}\hat{R}_i\hat{Y} = \hat{X}\hat{R}_i\hat{X}^{-1} = \hat{X}\hat{X}^{-1}\hat{R}_j\hat{X}\hat{X}^{-1} = \hat{E}\hat{R}_j\hat{E} = \hat{R}_j$).

Let us have some practice using our table. We have $\hat{X}^{-1}\hat{E}\hat{X} = \hat{X}^{-1}\hat{X}\hat{E} = \hat{E}\hat{E} = \hat{E}$ for each $\hat{X} \in G$, i.e. \hat{E} alone represents a class. Further, making $\hat{X}^{-1}\hat{A}\hat{X}$ for all possible \hat{X} gives:

$$\begin{aligned}\hat{E}^{-1}\hat{A}\hat{E} &= \hat{E}\hat{A}\hat{E} = \hat{A}\hat{E} = \hat{A}, \\ \hat{A}^{-1}\hat{A}\hat{A} &= \hat{A}\hat{A}\hat{A} = \hat{E}\hat{A} = \hat{A}, \\ \hat{B}^{-1}\hat{A}\hat{B} &= \hat{B}\hat{A}\hat{B} = \hat{F}\hat{B} = \hat{C}, \\ \hat{C}^{-1}\hat{A}\hat{C} &= \hat{C}\hat{A}\hat{C} = \hat{D}\hat{C} = \hat{B}, \\ \hat{D}^{-1}\hat{A}\hat{D} &= \hat{F}\hat{A}\hat{D} = \hat{B}\hat{D} = \hat{C}, \\ \hat{F}^{-1}\hat{A}\hat{F} &= \hat{D}\hat{A}\hat{F} = \hat{B}\hat{F} = \hat{C}.\end{aligned}$$

This means that \hat{A} belongs to the same class as \hat{B} and \hat{C} . Now we will create some conjugate elements to \hat{D} and \hat{F} :

$$\begin{aligned}\hat{A}^{-1}\hat{D}\hat{A} &= \hat{A}\hat{D}\hat{A} = \hat{B}\hat{A} = \hat{F}, \\ \hat{B}^{-1}\hat{D}\hat{B} &= \hat{B}\hat{D}\hat{B} = \hat{C}\hat{B} = \hat{F}, \\ \hat{C}^{-1}\hat{D}\hat{C} &= \hat{C}\hat{D}\hat{C} = \hat{A}\hat{C} = \hat{F},\end{aligned}$$

etc. Thus \hat{D} and \hat{F} make a class. Therefore the group under consideration consists of the following classes: $\{\hat{E}\}\{\hat{A}, \hat{B}, \hat{C}\}\{\hat{D}, \hat{F}\}$.

It is always like this: the group is the sum of the disjoint classes.

2 REPRESENTATIONS

A representation of the group is such a g -element sequence of square matrices (of the same dimension; a matrix is associated with each element of the group), that the matrices have a multiplication table consistent with the multiplication table of the group.

By consistency we mean the following. To each element of the group we assign a square matrix (of the same dimension for all elements). If the multiplication table for the group says that $\hat{R}_i \hat{R}_j = \hat{R}_k$, the matrix corresponding to \hat{R}_i times the matrix corresponding to \hat{R}_j is the matrix corresponding to \hat{R}_k . If this agrees for all \hat{R} , then we say that the matrices form a representation.¹⁵

We may create many group representations, see Table C.3.

The easiest thing is to see that Γ_1 satisfies the criterion of being a representation (the matrices have dimension 1, i.e. they are numbers). After looking for a while at Γ_2 we will say the same. Multiplying the corresponding matrices we will prove this for Γ_3 and Γ_4 . For example, for Γ_3 the product of the matrices \hat{B} and \hat{C} gives the matrix corresponding to operation \hat{D}

$$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}.$$

If we had more patience, we could show this equally easily for the whole multiplication table of the group. Note that

there are many representations of a group.

Note also an interesting thing. Let us take a point with coordinates $(x, y, 0)$ and see what will happen to it when symmetry operations are applied (the coordinate system rests, while the point itself moves). The identity operation \hat{E} leads to the following transformation matrix

$$\begin{bmatrix} x' \\ y' \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \end{bmatrix}$$

The results of the other operations are characterized by the following transformation matrices (you may check this step by step):

$$\begin{aligned} \hat{A}: \begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix} & \quad \hat{B}: \begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \quad \hat{C}: \begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \\ \hat{D}: \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} & \quad \hat{F}: \begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}. \end{aligned}$$

¹⁵ More formally: a representation is a *homomorphism of the group into the above set of matrices*.

Table C.3. Several representations of the equilateral triangle symmetry group

Repr.	Group elements					
	\hat{E}	\hat{A}	\hat{B}	\hat{C}	\hat{D}	\hat{F}
Γ_1	1	1	1	1	1	1
Γ_2	1	-1	-1	-1	1	1
Γ_3	$\begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 \\ 0 & 1 \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$
Γ_4	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} -1 & 0 & 0 \\ 0 & \frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ 0 & -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$	$\begin{bmatrix} 1 & 0 & 0 \\ 0 & -\frac{1}{2} & -\frac{\sqrt{3}}{2} \\ 0 & \frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix}$

Note that the matrices obtained are identical to those for the representation Γ_3 . Thus by transforming the coordinates of a point, we have generated a representation of the symmetry.

By transforming “anything” (coordinates of a point, vectors, functions) using the symmetry operations and collecting the results in the form of matrices, we always obtain a representation of the group.

Characters of representation

For any representation Γ , we may define vector $\chi^{(\Gamma)}$ of dimension g , having as elements the traces of the representation matrices $\Gamma(\hat{R}_i)$

$$\text{Tr } \Gamma = \sum_i \Gamma_{ii}, \quad (\text{C.3})$$

$$\chi^{(\Gamma)} \equiv \begin{bmatrix} \text{Tr } \Gamma(\hat{R}_1) \\ \text{Tr } \Gamma(\hat{R}_2) \\ \dots \\ \text{Tr } \Gamma(\hat{R}_g) \end{bmatrix} \equiv \begin{bmatrix} \chi^{(\Gamma)}(\hat{R}_1) \\ \chi^{(\Gamma)}(\hat{R}_2) \\ \dots \\ \chi^{(\Gamma)}(\hat{R}_g) \end{bmatrix}. \quad (\text{C.4})$$

The number $\chi^{(\Gamma)}(\hat{R}_i)$ is called the *character of representation* Γ that corresponds to operation \hat{R}_i . The characters of representations will play a most important role in the application of group theory to spectroscopy.

Irreducible representations

To explain what irreducible representation is, let us first define *reducible representations*.

reducible
representation

A representation is called *reducible* if its matrices can be transformed into what is called *block form* by using the transformation $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ for every matrix $\Gamma(\hat{R}_i)$, where \mathbf{P} is a non-singular matrix.

In block form the non-zero elements can only be in the square blocks located on the diagonal, Fig. C.3.

block form

If, using the same \mathbf{P} , we can transform each of the matrices $\Gamma(\hat{R}_i)$ and obtain the same block form, the representation is called *reducible*.

If we do not find such a matrix (because it does not exist), the representation is irreducible. If we carry out the transformation $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ (*similarity transformation*) for $i = 1, 2, \dots, g$ of a representation, the new matrices also form a representation Γ' called *equivalent* to Γ .

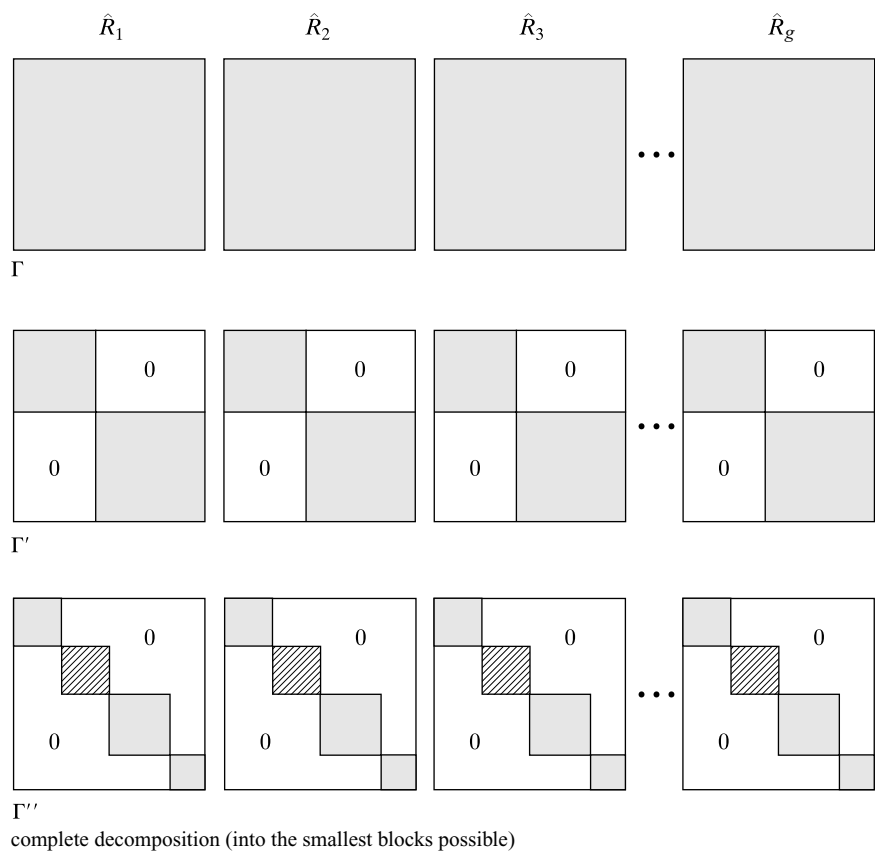


Fig. C.3. Reducible representation, block form and irreducible representation. In the first row the matrices $\Gamma(\hat{R}_i)$ are displayed which form a *reducible representation* (each matrix corresponds to the symmetry operation \hat{R}_i); the matrix elements are in general non-zero. The central row shows a representation Γ' equivalent to the first, i.e. related by a similarity transformation (through matrix \mathbf{P}); the new representation exhibits block form, i.e. in this particular case each matrix has two blocks of zeros, identical in all matrices. The last row shows an equivalent representation Γ'' that corresponds to the smallest square blocks (of non-zeros), i.e. the maximum number of blocks of identical form in all matrices. Not only Γ , Γ' and Γ'' are representations of the group, but also any sequence of individual blocks (as this shaded) is a representation. Thus, Γ'' is decomposed into the four irreducible representations.

This is easy to show. Indeed, group operations \hat{R}_i and \hat{R}_j correspond to matrices $\Gamma(\hat{R}_i)$ and $\Gamma(\hat{R}_j)$ in the original representation and to $\Gamma'(\hat{R}_i) = \mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}$ and $\Gamma'(\hat{R}_j) = \mathbf{P}^{-1}\Gamma(\hat{R}_j)\mathbf{P}$ in the equivalent representation (we will check in a moment whether this is indeed a representation). The product $\Gamma'(\hat{R}_i)\Gamma'(\hat{R}_j)$ equals to $\mathbf{P}^{-1}\Gamma(\hat{R}_i)\mathbf{P}\mathbf{P}^{-1}\Gamma(\hat{R}_j)\mathbf{P} = \mathbf{P}^{-1}\Gamma(\hat{R}_i)\Gamma(\hat{R}_j)\mathbf{P}$, i.e. to the matrix $\Gamma(\hat{R}_i)\Gamma(\hat{R}_j)$ transformed by *similarity transformation*, therefore everything goes with the same multiplication table. Thus matrices $\Gamma'(\hat{R}_i)$ also form a representation (Γ'). This means that we can create as many representations as we wish, it is sufficient to change

similarity
transformation

matrix P , and this is easy (since what we want is its singularity, i.e. the P^{-1} matrix has to exist).

The blocks are square matrices. It turns out that the set of the first blocks $\Gamma_1(\hat{R}_1), \Gamma_1(\hat{R}_2), \dots, \Gamma_1(\hat{R}_g)$ (each block for one operation) is a representation, the set of the second blocks $\Gamma_2(\hat{R}_1), \Gamma_2(\hat{R}_2), \dots, \Gamma_2(\hat{R}_g)$ forms a representation as well, etc. This is evident. It is sufficient to see what happens when we multiply two matrices in the same block form. The matrix product has the same block form and a particular block results from multiplication of the corresponding blocks of the matrices which are being multiplied.¹⁶

In particular, maximum decomposition into blocks leads, of course, to blocks that are no longer decomposable, and therefore are irreducible representations.

irreducible
representation

Properties of irreducible representations

For two irreducible representations α and β , the following *group orthogonality theorem* is satisfied:¹⁷

$$\sum_i [\Gamma^{(\alpha)}(\hat{R}_i)]_{mn} [\Gamma^{(\beta)}(\hat{R}_i)]_{m'n'}^* = \frac{g}{n_\alpha} \delta_{\alpha\beta} \delta_{mm'} \delta_{nn'}, \quad (\text{C.5})$$

where $\Gamma^{(\alpha)}(\hat{R})$ and $\Gamma^{(\beta)}(\hat{R})$ denote matrices that correspond to the group element \hat{R} (m, n and m', n' determine the elements of the matrices), the summation goes over all the group elements, and n_α is the dimension of the irreducible representation α , i.e. the dimension of the matrices which form the representation. The symbol $*$ means complex conjugation.¹⁸ We create two g -dimensional vec-

¹⁶Let us explain this by taking an example. We have two square matrices of dimension 4: A and B , both having the block form:

$$A = \begin{bmatrix} A_1 & \mathbf{0} \\ \mathbf{0} & A_2 \end{bmatrix}, \quad B = \begin{bmatrix} B_1 & \mathbf{0} \\ \mathbf{0} & B_2 \end{bmatrix} \quad \text{with}$$

$$A_1 = \begin{bmatrix} 3 & 1 \\ 1 & 2 \end{bmatrix}, \quad A_2 = \begin{bmatrix} 2 & 2 \\ 2 & 3 \end{bmatrix}, \quad B_1 = \begin{bmatrix} 1 & 3 \\ 3 & 2 \end{bmatrix}, \quad B_2 = \begin{bmatrix} 2 & 1 \\ 1 & 2 \end{bmatrix}.$$

Let us check that $C = AB$ has the same block form

$$C = \begin{bmatrix} C_1 & \mathbf{0} \\ \mathbf{0} & C_2 \end{bmatrix}$$

and that (which is particularly important for us) $C_1 = A_1 B_1$ and $C_2 = A_2 B_2$. Indeed, multiplying AB we have

$$C = \begin{bmatrix} 6 & 11 & 0 & 0 \\ 7 & 7 & 0 & 0 \\ 0 & 0 & 6 & 6 \\ 0 & 0 & 7 & 8 \end{bmatrix}, \quad \text{i.e.} \quad \begin{bmatrix} 6 & 11 \\ 7 & 7 \end{bmatrix} = C_1, \quad \begin{bmatrix} 6 & 6 \\ 7 & 8 \end{bmatrix} = C_2.$$

Hence, indeed $C_1 = A_1 B_1$ and $C_2 = A_2 B_2$.

¹⁷For the proof see H. Eyring, J. Walter, G.E. Kimball, "Quantum Chemistry", New York, Wiley (1944).

¹⁸It is important only for complex representations Γ .

tors: one composed of components $[\Gamma^{(\alpha)}(\hat{R}_i)]_{mn}$, the other from $[\Gamma^{(\beta)}(\hat{R}_i)]_{m'n'}^*$, $i = 1, 2, \dots, g$. Group orthogonality theorem says that

- if $\alpha \neq \beta$, the vectors are orthogonal,
- if $m \neq m'$ or $n \neq n'$, again the two vectors are orthogonal. The formula kills everything, except the two identical irreducible representations and we choose the same elements as the vector components.

Characters of irreducible representations

The most important consequence of the group orthogonality theorem is the equation:

$$\sum_i \chi^{(\alpha)}(\hat{R}_i) \chi^{(\beta)}(\hat{R}_i)^* = g \delta_{\alpha\beta}, \quad (\text{C.6})$$

where $\chi^{(\alpha)}(\hat{R}_i)$ is a character of the *irreducible representation* α corresponding to symmetry operation \hat{R}_i . Eq. (C.6), in view of eq. (C.4), may be rewritten as a scalar product in a unitary space (Appendix B)

$$\langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle = g \delta_{\alpha\beta}. \quad (\text{C.7})$$

Eq. (C.7) can be obtained from the group orthogonality theorem after setting $m = n$ and $m' = n'$, and summing over m and m' :

$$\begin{aligned} \langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle &= \sum_i \sum_m \sum_{m'} [\Gamma^{(\alpha)}(\hat{R}_i)]_{mm} [\Gamma^{(\beta)}(\hat{R}_i)]_{m'm'}^* \\ &= \frac{g}{n_\alpha} \delta_{\alpha\beta} \sum_m \sum_{m'} (\delta_{mm'})^2 = \frac{g}{n_\alpha} \delta_{\alpha\beta} n_\alpha = g \delta_{\alpha\beta}. \end{aligned}$$

Decomposing reducible representations into irreducible ones

It is important that

equivalent representations have identical characters,

because the trace of a matrix is invariant with respect to any similarity transformation. Indeed, for two equivalent representations Γ and Γ' , for any \hat{R}_i we have $\Gamma'(\hat{R}_i) = \mathbf{P}^{-1} \Gamma(\hat{R}_i) \mathbf{P}$, which gives

$$\begin{aligned} \chi^{(\Gamma')}(\hat{R}_i) &= \sum_m (\mathbf{P}^{-1} \Gamma(\hat{R}_i) \mathbf{P})_{mm} = \sum_{mkl} P_{mk}^{-1} \Gamma_{kl} P_{lm} = \sum_{kl} \Gamma_{kl} \sum_m P_{lm} P_{mk}^{-1} \\ &= \sum_{kl} \Gamma_{kl} (\mathbf{P} \mathbf{P}^{-1})_{lk} = \sum_{kl} \Gamma_{kl} \delta_{lk} = \sum_k \Gamma_{kk} = \chi^{(\Gamma)}(\hat{R}_i). \end{aligned}$$

In particular, the character of a representation is the same as its block form (with the maximum number of blocks, which correspond to irreducible representations):

$$\chi(\hat{R}_i) = \sum_{\alpha} a(\alpha) \chi^{(\alpha)}(\hat{R}_i), \quad (\text{C.8})$$

or, in other words,

$$\chi = \sum_{\alpha} a(\alpha) \chi^{(\alpha)}, \quad (\text{C.9})$$

where $a(\alpha)$ is a natural number telling us how many times the irreducible representation α appears in block form. The above formula comes from the very definition of the trace (the sum of the diagonal elements).

We will need another property of the characters. Namely,

the characters corresponding to the elements of a class are equal.

Indeed, two elements of group \hat{R}_i and \hat{R}_j which belong to the same class are related to one another by relation $\hat{R}_i = X^{-1} \hat{R}_j X$, where X is an element of the group. The same multiplication table is valid for the representations (from the definition of the representation), thus

$$\Gamma(\hat{R}_i) = \Gamma(X^{-1}) \Gamma(\hat{R}_j) \Gamma(X) = [\Gamma(X)]^{-1} \Gamma(\hat{R}_j) \Gamma(X). \quad (\text{C.10})$$

This concludes the proof, because here the matrices $\Gamma(\hat{R}_i)$ and $\Gamma(\hat{R}_j)$ are related by a similarity transformation, and therefore have identical characters. From now on we can write $\chi(C)$ instead of $\chi(\hat{R})$, where C denotes the class to which operation \hat{R}_i belongs.

Eq. (C.8) can be now modified appropriately. It can be rewritten as

$$\begin{aligned} \langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle &= \sum_C n_C \chi^{\alpha}(C) \chi^{\beta}(C)^* = \sum_C [\sqrt{n_C} \chi^{(\alpha)}(C)] [\sqrt{n_C} \chi^{(\beta)}(C)^*] \\ &= g \delta_{\alpha\beta}, \end{aligned} \quad (\text{C.11})$$

where C stands for the class, and n_C tells us how many operations belong to the class. This notation reminds us that the numbers $[\sqrt{n_C} \chi^{(\alpha)}(C)]$ for a fixed α and changing class C may be treated as the components of a vector (its dimension is equal to the number of classes) and that the vectors which correspond to different irreducible representations are orthogonal. The dimension of the vectors is equal to the number of classes, say, k . Since the number of orthogonal vectors, each of dimension k , cannot exceed k , then the number of the different irreducible representations is equal the number of classes.

In future applications it will be of key importance to find such a natural number $a(\alpha)$ which tells us how many times the irreducible representation α is encountered in a reducible representation. The formula for $a(\alpha)$ is the following

$$a(\alpha) = \frac{1}{g} \sum_C n_C \chi(C) \chi^{(\alpha)}(C)^*. \quad (\text{C.12})$$

The proof is simple. From the scalar product of both sides of eq. (C.9) with the vector $\chi^{(\beta)}$ after using eq. (C.7) we obtain

$$\langle \chi^{(\beta)} | \chi \rangle = \sum_{\alpha} a(\alpha) \langle \chi^{(\beta)} | \chi^{(\alpha)} \rangle = \sum_{\alpha} a(\alpha) g \delta_{\alpha\beta} = a(\beta) g \text{ or } a(\alpha) = \frac{1}{g} \langle \chi^{(\alpha)} | \chi \rangle.$$

This is the formula sought, because the characters are the same for all operations of the same class.

Note that

to find $a(\alpha)$ it is sufficient to know the *characters* of the representations, the representations themselves are not necessary.

Tables of characters of irreducible representations

Any textbook on the application of group theory in molecular spectroscopy contains tables of characters of irreducible representations which correspond to various symmetry groups of molecules.¹⁹

To apply group theory to a particular molecule, we first have to find the table of characters mentioned above. To this end:

- the Born–Oppenheimer approximation is used, therefore the positions of the nuclei are fixed in space (“geometry”),
- from the geometry, we make a list of all the symmetry operations which transform it into itself,
- we identify the corresponding symmetry group.²⁰

To find the proper table, we may use the Schoenflies notation for the symmetry²¹ (there are also some other notations):

\hat{E} the symbol of the identity operation (i.e. do nothing);

¹⁹The tables are constructed by considering possible symmetries (symmetry groups), creating suitable matrix representations, using similarity transformations to find the irreducible representations, by summing the diagonal elements, we obtain the required character tables.

²⁰This may be done by using a flow chart, e.g., given by P.W. Atkins, “*Physical Chemistry*”, sixth edition, Oxford University Press, Oxford, 1998.

²¹Artur Moritz Schoenflies (1853–1928), German mathematician, professor at the universities in Göttingen, Königsberg, Frankfurt am Main. Schoenflies proved (independently of J.S. Fiodorow and W. Barlow) the existence of the complete set of 230 space groups of crystals.

- \hat{C}_n rotation by angle $\frac{2\pi}{n}$ about the n -fold symmetry axis;
- \hat{C}_n^m rotation by $\frac{2\pi m}{n}$ about the n -fold symmetry axis;
- $\hat{\sigma}_v$ reflection in the plane through the axis of the highest symmetry;
- $\hat{\sigma}_h$ reflection in the plane perpendicular to the axis of the highest symmetry;
- \hat{i} inversion with respect to the centre of symmetry;
- \hat{S}_n rotation by angle $\frac{2\pi}{n}$ about the n -fold symmetry axis with subsequent reflection in the plane perpendicular to it;
- \hat{S}_n^m rotation by angle $\frac{2\pi m}{n}$ about the n -fold symmetry axis with subsequent reflection in the plane perpendicular to it.

The set of symmetry operations obtained forms the symmetry group. The symmetry groups also have their special symbols. The Schoenflies notation for the symmetry groups of some simple molecules is given in Table C.4 (their geometry corresponding to the energy minimum).

A molecule may be much more complicated, but often its symmetry is identical to that of a simple molecule (e.g., one of those reported in the table).

When we finally identify the table of characters suitable for the molecule under consideration, it is time to look at it carefully. For example, for the ammonia molecule we find the table of characters (Table C.5).

In the upper left corner the name of the group is displayed (C_{3v}). The symmetry operations are listed in the same row (in this case \hat{E} , $\hat{\sigma}_v$, \hat{C}_3).²² The operations are collected in classes, and the number of such operations in the class is given: the identity operation (\hat{E}) forms the first class, the three reflection operations (hence $3\hat{\sigma}_v$, previously called \hat{A} , \hat{B} , \hat{C}) corresponding to the planes which contain the threefold symmetry axis, *two* rotation operations (hence, $2\hat{C}_3$, previ-

Table C.4. Examples of the symmetry group (for a few molecules in their ground-state optimum geometry)

Molecule	Group
H ₂ O	C _{2v}
NH ₃	C _{3v}
CH ₄	T _d
benzene	D _{6h}
naphthalene	D _{2h}

Table C.5. C_{3v} group. Table of characters

C _{3v}	\hat{E}	$3\hat{\sigma}_v$	$2\hat{C}_3$		
A ₁	1	1	1	z	$x^2 + y^2, z^2$
A ₂	1	-1	1	R_z	
E	2	0	-1	$(x, y)(R_x, R_y)$	$(x^2 - y^2, xy)(xz, yz)$

²²The same symmetry operations as discussed on p. 911.

ously called \hat{D} and \hat{F}) about the threefold symmetry axis (by 120° and by 240° , or -120° , and the rotation by 360° is identical to \hat{E}).

We have information about the irreducible representations in the second and subsequent rows, one row for each representation. The number of irreducible representations is equal to the number of classes (three in our case), i.e. the table of characters is square. On the left-hand side we have the symbol of the representation telling us about its dimension (if the symbol is A, the dimension is 1, if it is E the dimension is 2, if T then 3). Thus, unfortunately, the letter E plays a double role in the table:²³ as the identity operation \hat{E} and as E – the symbol of an irreducible representation. In a given row (irreducible representation), the number below the symbol for class is the corresponding character. For the identity operation \hat{E} , the corresponding matrices are unit matrices, and the calculated character is therefore equal to the dimension of the irreducible representation.

The simplest representation possible is of great importance, all the characters equal 1 (in our case A_1). This will be called the fully symmetric representation.

Example 11. Decomposition of a reducible representation. Let us find how the reducible representation Γ_4 from p. 914 may be decomposed into irreducible representations. First we see from eq. (C.12) that characters rather than the representations themselves are required. The characters $\chi^{(\Gamma_4)}$ are calculated by summing up the diagonals of the matrix representations for the corresponding classes, $\chi^{(\Gamma_4)}$: 3 (class \hat{E}), -1 (class $\hat{\sigma}_v$), 0 (class \hat{C}_3). Let us first ask how many times (a_{A_1}) the irreducible representation A_1 is encountered in Γ_4 . The characters of A_1 (Table C.5) are: 1, 1, 1 for the corresponding classes. The number of the operations in the classes is respectively n_C : 1, 3, 2. From (C.12) we find $a(A_1) = \frac{1}{6}(1 \cdot 3 \cdot 1 + 3 \cdot (-1) \cdot 1 + 2 \cdot 0 \cdot 1) = 0$. Similarly we find $a(A_2) = \frac{1}{6}(1 \cdot 3 \cdot 1 + 3 \cdot (-1) \cdot (-1) + 2 \cdot 0 \cdot 1) = 1$ and $a(E) = \frac{1}{6}(1 \cdot 3 \cdot 2 + 3 \cdot (-1) \cdot 0 + 2 \cdot 0 \cdot (-1)) = 1$. Thus, we may write that $\Gamma_4 = A_2 + E$. This exercise will be of great help when the selection rules in spectroscopy are considered.

Projection operator on an irreducible representation

We will soon need information about whether a particular function exhibits certain symmetry properties in the system under consideration. We will need certain projection operators to do this.

$$\hat{P}^{(\alpha)} = \frac{n_\alpha}{g} \sum_i \chi^{(\alpha)*}(\hat{R}_i) \hat{R}_i \quad (\text{C.13})$$

represents the projection operator which projects onto the space of such functions which transform according to the irreducible representation $\Gamma^{(\alpha)}$.

²³This unfortunate traditional notation will not lead to trouble.

This means that either $\hat{P}^{(\alpha)} f$ transforms according to the irreducible representation $\Gamma^{(\alpha)}$ or we obtain zero. To be a projection operator, $\hat{P}^{(\alpha)}$ has to satisfy²⁴

$$\hat{P}^{(\alpha)} \hat{P}^{(\beta)} = \delta_{\alpha\beta} \hat{P}^{(\alpha)}. \quad (\text{C.14})$$

We can also prove that

$$\sum_{\alpha} \hat{P}^{(\alpha)} = 1, \quad (\text{C.15})$$

where the summation goes over all irreducible representations of the group.

²⁴This means that two functions which transform according to *different* irreducible representations are orthogonal, and that the projection of an already projected function changes nothing. Here is the proof. After noting that $\hat{R}\hat{S} = \hat{Q}$, or $\hat{S} = \hat{R}^{-1}\hat{Q}$ we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_{\alpha} n_{\beta}}{g^2} \sum_{\hat{R}, \hat{S}} \chi^{(\alpha)*}(\hat{R}) \chi^{(\beta)*}(\hat{S}) \hat{R} \hat{S} \\ &= \frac{n_{\alpha} n_{\beta}}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \chi^{(\alpha)*}(\hat{R}) \chi^{(\beta)*}(\hat{R}^{-1} \hat{Q}). \end{aligned}$$

Note, that

$$\chi^{(\beta)*}(\hat{R}^{-1} \hat{Q}) = \sum_k \Gamma_{kk}^{(\beta)*}(\hat{R}^{-1} \hat{Q}) = \sum_k \sum_l \Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) \Gamma_{lk}^{(\beta)*}(\hat{Q}).$$

After inserting this result we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_{\alpha} n_{\beta}}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \sum_m \Gamma_{mm}^{(\alpha)*}(\hat{R}) \sum_k \sum_l \Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) \Gamma_{lk}^{(\beta)*}(\hat{Q}) \\ &= \frac{n_{\alpha} n_{\beta}}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{\hat{R}} \sum_{k,l,m} \Gamma_{mm}^{(\alpha)*}(\hat{R}) \Gamma_{lk}^{(\beta)}(\hat{R}) \Gamma_{lk}^{(\beta)*}(\hat{Q}) \\ &= \frac{n_{\alpha} n_{\beta}}{g^2} \sum_{\hat{Q}} \hat{Q} \sum_{k,l,m} \Gamma_{lk}^{(\beta)*}(\hat{Q}) \sum_{\hat{R}} [\Gamma_{mm}^{(\alpha)*}(\hat{R}) \Gamma_{lk}^{(\beta)}(\hat{R})], \end{aligned}$$

because from the unitary character of the representation matrices $\Gamma^{(\beta)}(\hat{R}^{-1})$ and $\Gamma^{(\beta)}(\hat{R})$ we have $\Gamma_{kl}^{(\beta)*}(\hat{R}^{-1}) = \Gamma_{lk}^{(\beta)}(\hat{R})$. From the group theorem of orthogonality (eq. (C.5)) we have

$$\begin{aligned} \hat{P}^{(\alpha)} \hat{P}^{(\beta)} &= \frac{n_{\alpha} n_{\beta}}{g^2} \frac{g}{n_{\alpha}} \sum_{\hat{Q}} \hat{Q} \sum_{k,l,m} \Gamma_{lk}^{(\beta)*}(\hat{Q}) \delta_{ml} \delta_{mk} \delta_{\alpha\beta} \\ &= \delta_{\alpha\beta} \frac{n_{\alpha}}{g} \sum_{\hat{Q}} \hat{Q} \sum_m \Gamma_{mm}^{(\alpha)*}(\hat{Q}) \\ &= \delta_{\alpha\beta} \frac{n_{\alpha}}{g} \sum_{\hat{Q}} \chi^{(\alpha)*}(\hat{Q}) \hat{Q} = \delta_{\alpha\beta} \hat{P}^{(\alpha)}, \end{aligned}$$

as we wished to show, eq. (C.14).

The transformation of a function according to irreducible representation

The right-side of a character table (like Table C.5) contains the symbols x , y , z , $(x^2 - y^2, xy)$, R_x , R_y , R_z . These symbols will be needed to establish the selection rules in spectroscopy (UV-VIS, IR, Raman). They pertain to the coordinate system (the z axis coincides with the axis of highest symmetry). Let us leave the symbols R_x , R_y , R_z for a while.

We have some polynomials in the rows of the table. *The polynomials transform according to the irreducible representation which corresponds to the row.*²⁵ If a polynomial (displayed in a row of the table of characters) is subject to the projection $\hat{P}^{(\alpha)}$, then:

- if α does not correspond to the row, we obtain 0;
- if α corresponds to the row, we obtain either the polynomial itself (if the irreducible representation has dimension 1), or, if the dimension of the irreducible representation is greater than 1, a linear combination of the polynomials given in the same row (in parentheses).

If function f transforms according to a one-dimensional irreducible representation, the function is an eigenfunction of all the symmetry operators \hat{R} , with the corresponding eigenvalues $\chi^{(\alpha)}(\hat{R})$.

Let us come back to R_x , R_y , R_z . Imagine R_x , R_y , R_z as oriented circles perpendicular to a rotation axis (i.e. x , y or z) which symbolizes rotations about these axes. For example, operation \hat{E} and the two rotations \hat{C}_3 leave the circle R_z unchanged, while operations $\hat{\sigma}_v$ change its orientation to the opposite one, hence R_z transforms according to the irreducible representation A_2 . It turns out, that R_x and R_y transform into their linear combinations under the symmetry operations and therefore correspond to a two-dimensional irreducible representation (E).

3 GROUP THEORY AND QUANTUM MECHANICS

Representation basis

If we have two equivalent²⁶ nuclei in a molecule, this *always* results from a molecular symmetry, i.e. at least one symmetry operation exchanges the positions of these two nuclei. There is no reason at all that electrons should prefer one such nucleus rather than the other.²⁷ Let us focus on molecular orbitals calculated for a fully symmetric Fock operator.²⁸ Therefore,

²⁵Please recall the definition of the symmetry operation given on p. 907: $\hat{R}f(\mathbf{r}) = f(\mathbf{r})$, where $\hat{R}f(\mathbf{r}) = f(\hat{R}^{-1}\mathbf{r})$.

²⁶With respect to physical and chemical properties.

²⁷This may be not true for non-stationary states. The reason is simple. Imagine a long polymer molecule with two equivalent atoms at its ends. If one is touched by the tip of a tunnelling microscope and one electron is transferred to the polymer, a non-stationary asymmetric electron state is created.

²⁸Limiting ourselves to molecular orbitals is not essential.

each molecular orbital has to be such, that when it is squared the electron density is the same on the equivalent nuclei.

What will happen, however, to the *molecular orbital itself*? Squaring removes information about its sign. The signs of both atoms may be the same (symmetric orbital), but they may also be opposite²⁹ (antisymmetric orbital). For example, the bonding orbital for the hydrogen molecule is symmetric with respect to the reflection in the plane perpendicular to the internuclear axis³⁰ and passing through its centre, while the antibonding orbital is antisymmetric with respect to the operation.

We know how to apply symmetry operations on molecular orbitals (p. 908) and transform them to other functions.

Under such a symmetry operation the orbital either remains unchanged (like the bonding mentioned above), or changes sign (like the antibonding).

or, if the orbital level is degenerate, we may obtain a different function. This function corresponds to the same energy, because in applying any symmetry operation we only exchange equivalent nuclei, which are otherwise treated on an equal footing in the Hamiltonian.

²⁹This pertains to non-degenerate orbital levels. For a degenerate level any linear combination of the eigenfunctions (associated with the same level) is also an eigenfunction as good as those which entered the linear combination. A symmetry operation acting on an orbital gives another orbital corresponding to the same energy. In such a case, the squares of both orbitals in general does not exhibit the symmetry of the molecule. However, we can find such a linear combination of both, the square preserves the symmetry.

³⁰Let us see what it really means in a very *formal* way (it may help us in more complicated cases). The coordinate system is located in the middle of the internuclear distance (on the x axis, the internuclear distance equals $2A$). The bonding orbital $\varphi_1 = N_1(a + b)$ and the antibonding orbital $\varphi_2 = N_2(a - b)$, where N_1 and N_2 are the normalization constants, the $1s$ atomic orbitals have the following form

$$a \equiv \frac{1}{\sqrt{\pi}} \exp[-|\mathbf{r} - \mathbf{A}|] = \frac{1}{\sqrt{\pi}} \exp\left[-\sqrt{(x - A)^2 + y^2 + z^2}\right],$$

$$b \equiv \frac{1}{\sqrt{\pi}} \exp[-|\mathbf{r} + \mathbf{A}|] = \frac{1}{\sqrt{\pi}} \exp\left[-\sqrt{(x + A)^2 + y^2 + z^2}\right],$$

$$\mathbf{A} = (A, 0, 0).$$

The operator $\hat{\sigma}$ of the reflection in the plane $x = 0$ corresponds to the following unitary transformation matrix of the coordinates $U = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$. Therefore, the inverse matrix $U^{-1} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$, i.e. the transformation $U^{-1}\mathbf{r}$ means $x \rightarrow -x$, $y \rightarrow y$, $z \rightarrow z$, which transforms $a \rightarrow b$ and $b \rightarrow a$. Hence $\hat{\sigma}(a + b) = (b + a) = (a + b)$, $\hat{\sigma}(a - b) = (b - a) = -(a - b)$.

In both cases the molecular orbital represents an eigenfunction of the symmetry operator with eigenvalues $+1$ and -1 , respectively.

If we obtain another orbital (φ_2), then we may begin to play with it by applying all the symmetry operations. Some operations will lead to the same (new) orbital, sometimes with the opposite sign. After other operations we will obtain the old orbital φ_1 , sometimes with the opposite sign, and sometimes these operations will lead to a *third* orbital φ_3 . Then we apply the symmetry operations to the third orbital, etc. until the final set of orbitals is obtained which transform into themselves when subject to symmetry operations. The set of such linearly independent orbitals φ_i , $i = 1, \dots, n$, may be treated as the basis set in a vector space.

All the results of the application of operation $\hat{\mathcal{R}}_i$ on the orbitals φ_i are collected in a transformation matrix \mathbf{R}_i :

$$\hat{\mathcal{R}}_i \varphi = \mathbf{R}_i^T \varphi, \quad \text{where } \varphi = \begin{bmatrix} \varphi_1 \\ \dots \\ \varphi_n \end{bmatrix}. \quad (\text{C.16})$$

The matrices \mathbf{R}_i , $i = 1, 2, \dots, g$, form the n -dimensional representation (in general reducible) of the symmetry group of the molecule.

Indeed, let us see what happens if we apply operation $\hat{T} = \hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2$ to the function φ_i :

$$\hat{T} \varphi_i = (\hat{\mathcal{R}}_1 \hat{\mathcal{R}}_2) \varphi_i = \hat{\mathcal{R}}_1 \mathbf{R}_2^T \varphi = \mathbf{R}_2^T \hat{\mathcal{R}}_1 \varphi = \mathbf{R}_2^T \mathbf{R}_1^T \varphi = (\mathbf{R}_1 \mathbf{R}_2)^T \varphi.$$

This means that all the matrices \mathbf{R}_i form a representation.

BASIS OF A REPRESENTATION

The set of linearly independent functions φ_i , which served to create the representation, forms the *basis of the representation*.

The basis need not have been composed of the orbitals, it could be expressions like x , y , z or x^2 , y^2 , z^2 , xy , xz , yz or any linearly independent functions, provided they transform into themselves under symmetry operations. We may begin from an atomic orbital, and after applying symmetry operations will soon obtain a basis set which contains this orbital and all the other equivalent orbitals.

Decomposition of a function into irreducible representation components

Let us take a function f belonging to a Hilbert space. Since (see eq. (C.15)) $\sum_{\alpha} \hat{P}^{(\alpha)} = 1$, where α goes over all the irreducible representations of the group, f can be written as the sum of its components f_{α} , each component (belonging to the corresponding subspace of the Hilbert space) transforming according to the irreducible representation α

$$f = 1 \cdot f = \sum_{\alpha} \hat{P}^{(\alpha)} f = \sum_{\alpha} f_{\alpha}. \quad (\text{C.17})$$

In view of (C.14), components f_{α} and f_{β} are automatically orthogonal if $\alpha \neq \beta$.

Example 12. Decomposition of a function. Let us take three hydrogen atoms in the configuration of an equilateral triangle, and assume we are in the simplest version of the molecular orbitals in the LCAO MO approximation, i.e. the atomic basis set is composed of the three $1s$ orbitals a, b, c centred on the three nuclei. Let us check whether the following functions:

$$u_1 = a + b + c,$$

$$u_2 = b - c,$$

$$u_3 = a - c,$$

form the basis to a (reducible) representation. If symmetry operations are applied to a, b, c , they transform into each other (cf. Fig. C.2), and the results obtained are easily shown as linear combinations of the functions u_1, u_2, u_3 (with \mathbf{R}_i^T as transformation matrices). For example (see Table C.1, p. 911), $\hat{A}u_1 = a + b + c = u_1$, $\hat{A}u_2 = -b + c = -u_2$, $\hat{A}u_3 = a - b = -u_2 + u_3$. Hence,

$$\mathbf{A}^T = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & -1 & 1 \end{bmatrix}. \quad (\text{C.18})$$

In this way (see (C.16)) we obtain \mathbf{R}_i as:

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{A} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 0 & 1 \end{bmatrix}, \quad \mathbf{B} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & -1 & -1 \end{bmatrix}, \quad (\text{C.19})$$

$$\mathbf{C} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix}, \quad \mathbf{D} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & -1 \end{bmatrix}, \quad \mathbf{F} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & -1 \\ 0 & 1 & 0 \end{bmatrix}. \quad (\text{C.20})$$

Let us check that $\mathbf{DF} = \mathbf{E}$ and $\mathbf{AD} = \mathbf{B}$, i.e. exactly as for operations: $\hat{D}\hat{F} = \hat{E}$, $\hat{A}\hat{D} = \hat{B}$, and so on. Thus this is a representation, moreover, this is a representation *in a block form*, because u_1 always transforms within itself, while u_2 and u_3 mix between themselves. It can be shown that this mixing cannot be avoided by any choice of u . Hence, u_1 alone represents the basis of a one-dimensional irreducible representation (A_1 – this is seen from the characters corresponding to the first block 1×1), while u_2 and u_3 form the basis of a two-dimensional irreducible representation (E). Note that from the mathematical form of the functions u , it follows that u_2 and u_3 have to correspond to the same energy and this energy is different from that corresponding to u_1 . The conclusion is that a, b, c form the basis for a reducible representation, while their linear combinations u_1 and $\{u_2, u_3\}$ form the basis sets of two irreducible representations: A_1 and E. Any function which is a linear combination of a, b, c can also be represented as a linear combination of u_1, u_2, u_3 .

The same symmetry orbitals can be obtained using the projection operators (C.13). Let us take any of functions a, b, c (the result does not depend on this

choice), e.g., function a . In view of the beautiful equilateral triangle, such a function is no doubt a deformed object, which does not take the trouble to make the three vertices of the triangle equivalent. Let us see whether such a function has any component which transforms according to the irreducible representation A_1 . To this end, let us use the projection operator $\hat{P}^{(A_1)}$ (Table C.5 of characters on p. 921 and eq. (C.13)): $\hat{P}^{(A_1)}a = \frac{1}{6}(a + b + c + a + b + c) = \frac{1}{3}(a + b + c)$. There is thus a fully symmetric component³¹ in a . Now, let us use the same orbital a to obtain: $\hat{P}^{(A_2)}a = \frac{1}{6}(a + b + c - a - b - c) = 0$. This means that a does not contain anything which transforms according to A_2 . Now it is the turn of the irreducible representation E: $\hat{P}^{(E)}a = \frac{2}{6}(2a - b - c + 0 \cdot a + 0 \cdot b + 0 \cdot c) = \frac{1}{3}[2(a - c) - (b - c)]$. We have now obtained is a linear combination of u_2 and u_3 .

If the projections were made for function b , we would obtain a trivial repetition³² for the irreducible representations A_1 and A_2 and a non-trivial result for the irreducible representation E: $\hat{P}^{(E)}b = \frac{2}{6}(2b - a - c + 0 \cdot a + 0 \cdot b + 0 \cdot c) = \frac{1}{3}[2(b - c) - (a - c)]$, which is just another linear combination of u_2 and u_3 . These two functions are therefore inseparable and form the basis for a two-dimensional *irreducible* representation.

DECOMPOSITION INTO IRREDUCIBLE REPRESENTATIONS

Any function that is a linear combination of the basis functions of a *reducible* representation can be decomposed into a linear combination of the basis functions of those *irreducible* representations which form the reducible representation.

Most important

MOST IMPORTANT...

The wavefunctions corresponding to an energy level

- *form the basis of an irreducible representation* of the symmetry group of the molecule, or in other words, transform according to this irreducible representation
- the dimension of the representation is equal to the degeneracy of the energy level.

This is how it should be, because if a symmetry operation acts on an eigenfunction of the Hamiltonian, we will have only two possible results: 1) we obtain the same function to the accuracy of the sign (in the case of a one-dimensional representation, by definition irreducible); 2) another function *corresponding to the*

³¹This sentence carries a simple message, that by mixing symmetric objects we may obtain an asymmetric object, e.g., the asymmetric function $a + 2b$ can be represented by the linear combination $u_1 + u_2$, both functions transforming according to an irreducible representation of the symmetry group.

³² $\hat{P}^{(A_1)}b = \frac{1}{3}(a + b + c)$ and $\hat{P}^{(A_2)}b = 0$.

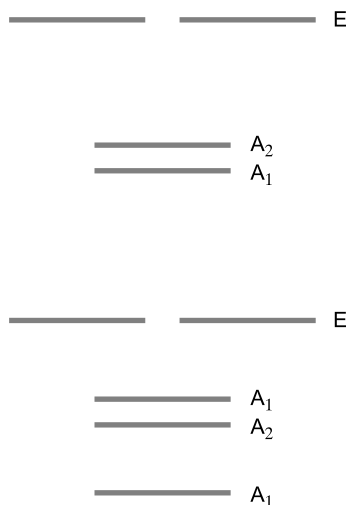


Fig. C.4. Each energy level corresponds to an irreducible representation of the symmetry group of the Hamiltonian. Its linearly independent eigenfunctions corresponding to a given level form the basis of the irreducible representation, or in other words, transform according to this representation. The number of the basis functions is equal to the degeneracy of the level.

same energy (because of the same physical situation). Acting on the function obtained and repeating the whole procedure, we will finally arrive at a set of n linearly independent functions which correspond to the same energy (the basis of a n -dimensional irreducible representation).

This means (Fig. C.4) that

the energy levels may be labelled, each label corresponding to a single irreducible representation.

Eugene Wigner was the first who obtained this result. This will be of fundamental importance when the selection rules in spectroscopy will be considered.

We usually have plenty of energy levels, while the number of irreducible representations is small. Thus, in general there will be many levels with the same label. Group theory will never tell us either how many levels correspond to a particular irreducible representation, or to what energy they correspond.

4 INTEGRALS IMPORTANT IN SPECTROSCOPY

Direct product of the irreducible representations

We are quickly approaching the application of group theory to optical transitions in spectroscopy. The most important issue here will be a decision as to whether an integral is zero or non-zero. If the integral is zero, the transition is forbidden, if it is non-zero, it is allowed. To make such a decision we have to use what is known as the *direct product of irreducible representations*. Imagine basis functions $\{\varphi_i\}$ and $\{\psi_j\}$ which correspond to irreducible representations α and β of the symmetry group of a molecule. Let us make a set $\{\varphi_i\psi_j\}$ of all their possible products (i.e. the Cartesian product).

DIRECT PRODUCT

The products $\{\varphi_i \psi_j\}$ when subject to symmetry operations, lead (as usual) to a representation, and this representation is called the *direct product* $\Gamma^\alpha \times \Gamma^\beta$ of the irreducible representations Γ^α and Γ^β .

The functions $\{\varphi_i \psi_j\}$ form the basis set of a representation (reducible in general). The matrices of the representations we obtain as usual by applying symmetry operations (eq. (C.16)):

$$\begin{aligned}\hat{R}[\varphi_i(\mathbf{r})\psi_j(\mathbf{r})] &= \varphi_i(\hat{R}^{-1}\mathbf{r})\psi_j(\hat{R}^{-1}\mathbf{r}) = \sum_k \Gamma_{ki}^{(\alpha)} \varphi_k \sum_l \Gamma_{lj}^{(\beta)} \psi_l \\ &= \sum_{kl} \Gamma_{ki}^{(\alpha)} \Gamma_{lj}^{(\beta)} \varphi_k \psi_l = \sum_{kl} Z_{ij,kl} \varphi_k \psi_l,\end{aligned}$$

where $\Gamma_{ki}^{(\gamma)}$ are the matrix elements of the irreducible representation γ , $Z_{ij,kl} = \Gamma_{ki}^{(\alpha)} \Gamma_{lj}^{(\beta)}$. Of course,

the dimension of this representation is the product of the dimensions of the representations α and β , because this is the number of the functions $\varphi_k \psi_l$.

The characters $\chi^{(\alpha \times \beta)}$ of the representation can easily be obtained from the characters of the irreducible representations, we just have to multiply the latter:

$$\chi^{(\alpha \times \beta)}(\hat{R}) = \chi^{(\alpha)}(\hat{R}) \chi^{(\beta)}(\hat{R}). \quad (\text{C.21})$$

Indeed, the formula is justified by:

$$\begin{aligned}\chi^{(\alpha \times \beta)}(\hat{R}) &= \sum_{kl} Z_{kl,kl} = \sum_{kl} \Gamma_{kk}^{(\alpha)} \Gamma_{ll}^{(\beta)} = \left(\sum_k \Gamma_{kk}^{(\alpha)} \right) \left(\sum_l \Gamma_{ll}^{(\beta)} \right) \\ &= \chi^{(\alpha)}(\hat{R}) \chi^{(\beta)}(\hat{R}).\end{aligned} \quad (\text{C.22})$$

This rule can be naturally generalized for higher number of irreducible representations in the direct product (just multiply the characters of the irreducible representations). In a while we will have the product of three irreducible representations.

When is an integral bound to be zero?

Everyone studying this book should know how to calculate the integral

$$\int_{-1}^{+1} x \, dx = \left[\frac{x^2}{2} \right]_{-1}^{+1} = \frac{1}{2} - \frac{1}{2} = 0.$$

Note, however, that we can tell what the value of the integral is without any calculation, just by looking at the integrand. Indeed, the integrand is odd with respect to

the transformation $x \rightarrow -x$, i.e. the plot of the integral is an antisymmetric function with respect to the reflection in the plane perpendicular to x at $x = 0$. The integration limits are symmetric with respect to that point. An integral means the area under the plot, therefore what we gain for $x > 0$, we lose for $x < 0$ and the integral will be exactly zero.

The force of group theory relies, even with a complicated integrands, on being able to tell immediately whether the integral is equal to zero. This allows us to predict whether an optical transition is allowed or forbidden.

We have to stress that these conclusions will be valid independent of the approximations used to calculate the molecular wave functions. The reason is that they follow from the symmetry, which is identical for exact and approximate wave functions.

The previous example can be generalized. Let us take the integral

$$\int f_{\alpha} f_{\beta} f_{\gamma} \dots d\tau, \quad (\text{C.23})$$

where $f_{\alpha}, f_{\beta}, f_{\gamma}, \dots$ transform according to the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$, of a symmetry group, and the integration is over the whole space.

WHEN IS THE INTEGRAL EQUAL TO ZERO?

If a representation (in general reducible), being the direct product of the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$ does not contain the fully symmetric representation (its all characters are equal to 1), the integral is equal to zero.

This is precisely our goal in this Appendix and this is why we have been working so hard with symmetry groups, operations, characters, etc. The essence of the theorem is very simple. The product $f_{\alpha} f_{\beta} f_{\gamma} \dots$ transforms according to the (in general *reducible*) representation, which is the direct product of the irreducible representations $\Gamma^{(\alpha)}, \Gamma^{(\beta)}, \Gamma^{(\gamma)}, \dots$. This means that according to eq. (C.17) the integrand $f_{\alpha} f_{\beta} f_{\gamma} \dots$ can be represented as a linear combination of the basis functions of all the irreducible representations: $f_{\alpha} f_{\beta} f_{\gamma} \dots = \sum_{\mu} g_{\mu}$, where g_{μ} transforms according to the irreducible representation $\Gamma^{(\mu)}$. Therefore, the integral (C.23) is the sum of the integrals

$$\int f_{\alpha} f_{\beta} f_{\gamma} \dots d\tau = \sum_{\mu} \int g_{\mu} d\tau. \quad (\text{C.24})$$

Let us take one such integral: $\int g_{\mu} d\tau$. Note that the integration is over the whole space (i.e. the integration limits are symmetric). If the integrand g_{μ} were antisymmetric with respect to one or more symmetry operations, the integral would automatically be zero (the same argument as for $\int x dx$). From this it follows that

all integrals in the sum would be zero except the single one which contains the integrand transforming according to the fully symmetric representation.³³

There are two (important to us) special cases of this theorem.

Two special cases

$\int f_\alpha f_\beta d\tau = \delta_{\alpha\beta} A$, i.e. in order for the integral not to vanish we have to have: $\Gamma^{(\alpha)} = \Gamma^{(\beta)}$.

The proof is very simple and relies on the fact that the characters of the fully symmetric irreducible representation are equal to 1. The number of times, $a(A)$, the fully symmetric representation A , is present in the direct product $\Gamma^{(\alpha)} \times \Gamma^{(\beta)}$, we calculate from the formula:

$$\begin{aligned} a(A) &= \frac{1}{g} \sum_i \chi^{(\alpha \times \beta)}(\hat{R}_i) \chi^{(A)}(\hat{R}_i)^* = \frac{1}{g} \sum_i \chi^{(\alpha \times \beta)}(\hat{R}_i) \\ &= \frac{1}{g} \sum_i \chi^{(\alpha)}(\hat{R}_i) \chi^{(\beta)}(\hat{R}_i)^* = \delta_{\alpha\beta}. \end{aligned} \quad (C.25)$$

This means that the fully symmetric representation is always present in $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$ and therefore the integral does not vanish.³⁴

Let us take the integral

$$\int f_\alpha f_\beta f_\gamma d\tau, \quad (C.26)$$

where $f_\alpha, f_\beta, f_\gamma$ transform according to the irreducible representations α, β, γ . For the integral not to vanish the direct product $\Gamma^{(\alpha)} \times \Gamma^{(\beta)}$ has to contain the representation $\Gamma^{(\gamma)}$.

This means that to have integral (C.26) not vanish, the function $f_\alpha f_\beta$ decomposes (eq. (C.17)) in such a way that there is a non-zero component belonging to $\Gamma^{(\gamma)}$. If this happens, according to the previous case, a component of the integrand will transform according to the fully symmetric representation, which will save the integral (C.26) from vanishing.

Selection rules for electronic transitions (UV-VIS)

The selection rules will be shown taking the example of pyrazine and its mono- and diprotonated ions (Fig. C.5).

³³Only for the fully symmetric representation are all the characters equal to 1, and therefore the corresponding function does not change under symmetry operations.

³⁴This is easy to understand. What transforms, according to $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$, is the product of two (in general different) functions, each belonging to $\Gamma^{(\alpha)}$. It means that the function behaves in a very special way (typical for $\Gamma^{(\alpha)}$) under symmetry operations, e.g., changes sign under \hat{R}_1 , while other operations leave it unchanged. If we have a product of two such functions, this means the product does not change at all under \hat{R}_1 (and, of course, the other operations), i.e. transforms according to the fully symmetric operation. This is why the fully symmetric representation is always present in $\Gamma^{(\alpha)} \times \Gamma^{(\alpha)}$.

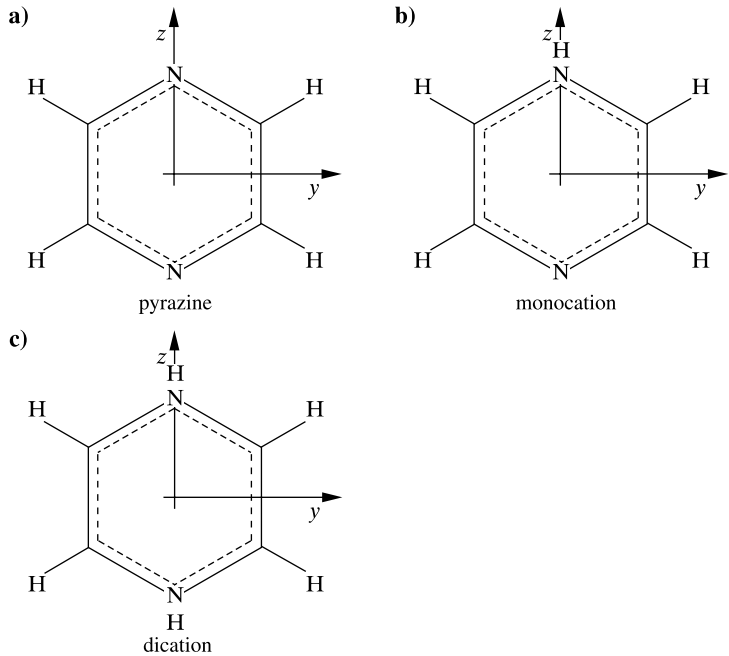


Fig. C.5. Pyrazine (a) and its mono- (b) and diprotonated (c) derivatives. The x axis is perpendicular to the ring plane, the y axis is in the ring plane perpendicular to the NN axis, and z is the NN axis.

A glimpse at the chemical formulae is sufficient to tell that the monocation of pyrazine has the same symmetry as H_2O , which corresponds to symmetry group C_{2v} (see Table C.4), while pyrazine and its diprotonated derivative have the symmetry identical with that of naphthalene, i.e. D_{2h} . Let us focus first on the last case.

Example 13. Pyrazine and its diprotonated derivative. Every book on group theory contains a table of characters of the symmetry group D_{2h} (Table C.6, x axis perpendicular to the plane of the molecule, z goes through the nitrogen atoms).

Table C.6. D_{2h} group table of characters

D_{2h}	\hat{E}	$\hat{C}_2(z)$	$\hat{C}_2(y)$	$\hat{C}_2(x)$	\hat{i}	$\hat{\sigma}(xy)$	$\hat{\sigma}(xz)$	$\hat{\sigma}(yz)$	
A_g	1	1	1	1	1	1	1	1	x^2, y^2, z^2
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	z
B_{2u}	1	-1	1	-1	-1	1	-1	1	y
B_{3u}	1	-1	-1	1	-1	1	1	-1	x

From Table C.6 we see³⁵ that what we call irreducible representations are simply the *distinct rhythms* of pluses and minuses, which after squaring, give the fully symmetric behaviour. All the electronic states of pyrazine and its diprotonated derivative can be described by the irreducible representation labels: $A_g, B_{1g}, B_{2g}, B_{3g}, A_u, B_{1u}, B_{2u}, B_{3u}$.

We may ask: what are the selection rules for state-to-state optical transitions? Are all transitions allowed, or are some of them forbidden? From the theory of the electromagnetic field (cf. Chapters 7 and 12) it follows that the probability of the transition between states k and l is proportional to $|\mu_{kl}(x)|^2$ or to $|\mu_{kl}(y)|^2$ or to $|\mu_{kl}(z)|^2$, respectively,³⁶ depending on the electromagnetic wave polarization along axes x , y or z axes, with:

$$\begin{aligned}\mu_{kl}(x) &= \int \psi_k^* \hat{\mu}_x \psi_l d\tau, \\ \mu_{kl}(y) &= \int \psi_k^* \hat{\mu}_y \psi_l d\tau, \\ \mu_{kl}(z) &= \int \psi_k^* \hat{\mu}_z \psi_l d\tau,\end{aligned}\tag{C.27}$$

where ψ stands for the electronic states k , and l [eq. (6.8) on p. 225], $\hat{\mu}_x, \hat{\mu}_y, \hat{\mu}_z$ are the operators of the molecular dipole moment components,³⁷ e.g.,

$$\hat{\mu}_z = \sum_i q_i z_i,$$

q_i is the electric charge of the particle (electron or nucleus) having its z component equal to z_i . Since we will decide, by using group theory, whether this integral³⁸ vanishes or not, the important thing is that μ_x transforms in exactly the same way as the coordinate x . The integrand $\psi_k^* \hat{\mu}_x \psi_l$ transforms as the direct product of the three irreducible representations: that of ψ_k , that of $\hat{\mu}_x$ and that of ψ_l .

Excitations from the ground-state

Suppose we

- have a molecule in its ground-state ψ_k (thus, belonging to the fully symmetric irreducible representation A_g),

³⁵Note that all the irreducible representations of the symmetry group of the molecules under consideration are one-dimensional, hence their energy levels are non-degenerate.

³⁶From the equality $|\mu_{kl}(x)|^2 = |\mu_{lk}(x)|^2$ and similarly for y and z , it follows that the optical excitation and the corresponding emission have the same probability.

³⁷This may look alarming, because the operator depends on the choice of the coordinate system (cf. Appendix X). Do not worry, everything is all right. Even if the dipole moment depends on such a choice, any two choices give dipole moments differing by a *constant vector*. This vector being a constant can be shifted outside the integral and the integral itself will become zero, because ψ_k and ψ_l are orthogonal. Thus, to our delight, light absorption does not depend on the choice of the coordinate system. This is fine.

³⁸The integration goes over all the electronic coordinates.

- immobilize the molecule in space (say, in a crystal),
- introduce the coordinate system in the way described above,
- irradiate the molecule with light polarized along the x axis

and ask *which states will the molecule be excited to*. The direct product of A_g and the irreducible representation to which x belongs, decomposes into some irreducible representations. For the optical transition to be allowed, we have to find among them the irreducible representation to which ψ_l belongs (just recall that $\int f_\alpha f_\beta d\tau = \delta_{\alpha\beta} A$). Only then will the integrand contain something that has the chance to transform according to the fully symmetric representation. The x coordinate belongs to the representation B_{3u} (see Table C.6, last column). Therefore, let us see what represents the direct product $A_g \times B_{3u}$. We have eq. (C.12) for the integer $a(\alpha)$ that is the number of irreducible representations α in a given reducible representation. Let us calculate this number for the representation (in general reducible) being the direct product, and all the irreducible representations α . In this particular case the direct product is³⁹ $A_g \times B_{3u}$. We have

polarization x

$$\begin{aligned} a(A_g) &= \frac{1}{8}[1 \times 1 + 1 \times (-1) + 1 \times (-1) + 1 \times 1 + 1 \times (-1) + 1 \times 1 \\ &\quad + 1 \times 1 + 1 \times (-1)] = 0, \\ a(B_{1g}) &= \frac{1}{8}[1 \times 1 + 1 \times (-1) + (-1) \times (-1) + (-1) \times 1 \\ &\quad + 1 \times (-1) + 1 \times 1 + (-1) \times 1 + (-1) \times (-1)], \\ &= 0 \end{aligned}$$

etc., all zeros, and finally

$$\begin{aligned} a(B_{3u}) &= \frac{1}{8}[1 \times 1 + (-1) \times (-1) + (-1) \times (-1) + 1 \times 1 + (-1) \times (-1) + 1 \times 1 \\ &\quad + 1 \times 1 + (-1) \times (-1)] = 1, \end{aligned}$$

exactly as we have expected. Thus, we can write⁴⁰

$$A_g \times B_{3u} = B_{3u}.$$

³⁹The characters of $A_g \times B_{3u}$ are as follows (in order of the symmetry operations in the table of characters):

$$1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad 1 \quad -1$$

i.e. they are identical to those of the (it turns out irreducible) representation B_{3u} . Such a product is really easy to form. In the table of characters one finger goes horizontally over the characters of A_g (they are all equal to 1), while the second finger moves similarly over the characters of B_{3u} and we multiply what the first finger shows by what the second finger shows. The result is the character of the direct product $A_g \times B_{3u}$, which in this case turns out to be exactly the character of B_{3u} . This is why we may expect that $a(\alpha)$ will all be zero except $a(B_{3u}) = 1$.

⁴⁰We may say that the fully symmetric representation plays the role of unity in the multiplication of irreducible representations.

Now only those ψ_l are allowed in optical transitions (from the ground state A_g) that are labelled by B_{3u} , because only the direct product $B_{3u} \times B_{3u}$ may contain the fully symmetric irreducible representation A_g . Thus, the transitions $A_g \Rightarrow B_{3u}$ as well as $B_{3u} \Rightarrow A_g$ are allowed, if the light is polarized along x , i.e. perpendicular to the ring of the molecule.

polarization y

Now let us take light polarized along y , i.e. within the molecular plane, perpendicularly to the N–N line. This time we are interested in the irreducible representations that arise from $A_g \times B_{2u}$, because y transforms according to B_{2u} . Very similarly [by analyzing $a(\alpha)$] we find that

$$A_g \times B_{2u} = B_{2u}.$$

This means that the allowed states are now of the B_{2u} type.

polarization z

Similarly, for polarization along z (z belongs to B_{1u}), i.e. along the nitrogen–nitrogen direction, we have

$$A_g \times B_{1u} = B_{1u}.$$

Thus for polarization parallel to the NN axis of the molecule, absorption may occur from the ground state to any state of the B_{1u} type (and *vice versa*).

transition
moment

Nothing more can be said when relying solely on group theory. We will not get any information about the energies of the transitions, or about the corresponding intensities. To get this additional (and important) information we have work hard to solve the Schrödinger equation, rather than count on some easy profits obtained by the primitive multiplication of integers (as in group theory). To obtain the intensities, we have to calculate the transition moment integrals μ_{kl} . However, group theory, by excluding from the spectrum *many transitions* (forbidden ones), provides a lot of important information on the molecule. Table C.7 collects the calculated light frequencies⁴¹ ($\bar{\nu}$ in wavenumbers, or cm^{-1} , $\nu = c\bar{\nu}$, where ν is the usual frequency), the *oscillator strengths* f_{kl} (in a.u.)

$$f_{kl} = \frac{4\pi c}{3} \nu |\mu_{kl}|^2, \quad (\text{C.28})$$

as well as the polarization of light for excitations from the electronic ground state for pyrazine and the pyrazine monocation. It is seen that the left-hand side of Table C.7 is consistent with the selection rules derived above. Indeed, a large f_{kl} only corresponds to those transitions from the ground state of the pyrazine that have been predicted as allowed (B_{1u} , B_{2u} and B_{3u}). The predicted polarization also agrees with the observed polarization.

oscillator
strength

Excitations from an excited state

Calculations for absorption from the ground-state were particularly simple. Now let us see whether anything will be more complicated for the transitions from an excited state of the B_{2g} type of symmetry. We are going to calculate $a(\alpha)$ (for every α) for the following representations:

⁴¹J. Koput, unpublished results.

Table C.7. Wave numbers ($\bar{\nu}$), oscillator strengths (f_{kl}) and light polarization (in parentheses)

Pyrazine			Pyrazine monocation		
Excited state	$\bar{\nu}$	f_{kl}	Excited state	$\bar{\nu}$	f_{kl}
B _{3u}	28960	0.015(<i>x</i>)	B ₁	27440	0.007(<i>x</i>)
B _{2u}	36890	0.194(<i>y</i>)	B ₂	34130	0.280(<i>y</i>)
B _{2g}	38890	0.0	A ₂	45100	0.0
A _u	41710	0.0	A ₁	49720	0.126(<i>z</i>)
B _{1u}	49800	0.183(<i>z</i>)	B ₁	57380	0.012(<i>x</i>)
B _{1g}	57070	0.0	A ₂	57710	0.0
B _{1u}	57420	0.426(<i>z</i>)	A ₁	58210	0.625(<i>z</i>)
A _u	60170	0.0	A ₂	59830	0.0
B _{2g}	60970	0.0	B ₂	60370	0.010(<i>y</i>)

for polarization along *x*: B_{2g} × B_{3u}
 for polarization along *y*: B_{2g} × B_{2u}
 for polarization along *z*: B_{2g} × B_{1u}.

The characters of the representation B_{2g} × B_{3u} are the following (Table C.6, the first finger goes along B_{2g}, the second – along B_{3u}, etc.)

$$1 \quad -1 \quad -1 \quad -1 \quad -1 \quad 1 \quad 1$$

and are identical with the characters of B_{1u}. Hence, even without any calculation of $a(\alpha)$, we have B_{2g} × B_{3u} = B_{1u}. Thus the transitions (for the polarization along *x*) are allowed only for the states labelled by B_{1u}, because otherwise there is no chance of obtaining a fully symmetric integrand. Similarly, by multiplying B_{2g} and B_{2u} we obtain the following characters of B_{2g} × B_{2u}:

$$1 \quad 1 \quad 1 \quad 1 \quad -1 \quad -1 \quad -1 \quad -1$$

and these are identical to the characters of A_u, therefore B_{2g} × B_{2u} = A_u. If the polarization of light is along *y*, the only excitations (or deexcitations) possible are for states belonging to A_u. Finally, for polarization along *z*, we find the characters of B_{2g} × B_{1u}:

$$1 \quad -1 \quad -1 \quad 1 \quad -1 \quad 1 \quad 1 \quad -1$$

that turn out to be those of B_{3u}. This means that B_{2g} × B_{1u} = B_{3u} and that the transitions are possible only for states belonging to B_{3u}.

Example 14. Pyrazine monocation. As to the selection rules, nothing was said so far about the pyrazine monocation. We will be interested in excitations from the electronic ground state (as in Table C.7). The pyrazine monocation corresponds to symmetry group C_{2v} (Table C.8).

The ground state belongs to the fully symmetric irreducible representation A₁. Since (as before) we begin by excitations from the ground state, let us see which irreducible representations arise from A₁ × B₁ (for the *x* polarization of light, see Table C.8, *x* transforms according to B₁), A₁ × B₂ (for the *y* polarization)

Table C.8. C_{2v} group characters

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, R_x	yz

and $A_1 \times A_1$ (for the z polarization). We calculate the characters of $A_1 \times B_1$ by multiplying 1 by

$$1 \quad -1 \quad 1 \quad -1,$$

and checking in Table C.8 that these correspond to B_1 (it has to be like this, because the characters of A_1 are all equal to 1), i.e. $A_1 \times B_1 = B_1$. Similarly, even without immediate checking, we see that $A_1 \times B_2 = B_2$ and $A_1 \times A_1 = A_1$. In this way the following allowed transitions from the ground state (A_1) have been predicted:

for polarization along x : $A_1 \rightarrow B_1$
 for polarization along y : $A_1 \rightarrow B_2$
 for polarization along z : $A_1 \rightarrow A_1$.

This agrees with $f_{kl} \neq 0$ values of Table C.7.

Now we are able to compare the spectrum for pyrazine and for its monocation, Table C.7. Attaching a proton to the pyrazine (creating its monocation) does not look like something that would ruin the UV-VIS spectrum. We might expect that the frequencies of the bands, even their intensities should be somehow similar in both molecules. As we can see from the Table, the frequencies are similar indeed. For both molecules there are forbidden ($f_{kl} = 0$) and allowed ($f_{kl} \neq 0$) transitions. Note that what is allowed for the pyrazine is also allowed for its cation, the light polarization coincides, even the values of f_{kl} are similar (we have taken into account that the transition to B_{1u} in pyrazine with frequency 49800 cm^{-1} corresponds to the transition to A_1 in the monocation with frequency 49720 cm^{-1}). In the monocation there are some additional transitions allowed: to B_1 and to B_2 . This is quite understandable, because the number of symmetry operations for the monocation is smaller, and the higher molecular symmetry the more numerous are forbidden transitions. If a molecule had no symmetry operations at all (except of course the identity symmetry), then all transitions would be allowed.

Thus, practically with zero effort, we find the selection rules in UV-VIS for any molecule we want.

Selection rules in IR and Raman spectra

The selection rules derived above pertain to electronic transitions, when the positions of the nuclei are fixed in space. Now a vibrational excitation of the molecule will be considered, while the electronic state is assumed to be unchanged. The vibrations of a molecule are related to its vibrational levels (each corresponding to an irreducible representation) and the corresponding vibrational wave functions,

We assume that small atomic deviations satisfy the symmetry requirements of the symmetry group of the molecule (valid for all atoms in equilibrium positions) and transform according to the irreducible representation, to which the normal mode belongs. Squaring the deviations destroys information about their signs, i.e. the absolute values of the deviations of the equivalent atoms are the same. This means that the squares of deviations transform according to the fully symmetric representation of the group.

To establish the vibrational selection rules, let us first define the vibrational states of $3N - 6$ harmonic oscillators (normal modes). The ground state of the system is no doubt the state in which *every* normal mode i is in its ground state, $\psi_{i,0}$. The ground-state wave function of the i -th normal mode reads as (p. 166)

$$\psi_{i,0} = N_0 \exp(-a_i Q_i^2), \quad (\text{C.29})$$

where $a_i > 0$ is a constant, and Q_i is the normal mode coordinate. Whatever this normal mode is, the wave function contains the *square* of Q_i , i.e. the sign of the deviations of the equivalent atoms *is irrelevant*.

The squares of the deviations, and therefore function $\psi_{i,0}$ itself, transform independently of i .

Let us denote this fully symmetric irreducible representation by A_1 . The wavefunction of the first *excited state* of a normal mode has the form (p. 166)

$$\psi_{i,1} = N_1 Q_i \exp(-a_i Q_i^2) \quad (\text{C.30})$$

and we see that $\psi_{i,1}$ transforms exactly as the coordinate Q_i does, i.e. according to the irreducible representation to which the normal mode belongs (because Q_i^2 in the exponent and therefore the exponent itself both belong to the fully symmetric representation). In the harmonic approximation the total vibrational wavefunction of the system of $3N - 6$ normal (i.e. independent) oscillators can be written as:

$$\psi_0^{\text{osc}} = \psi_{1,0} \psi_{2,0} \psi_{3,0} \dots \psi_{3N-6,0}, \quad (\text{C.31})$$

the zeros in the indices mean that all the modes are in their ground states. This means that ψ_0^{osc} transforms according to the representation being the direct product $A_1 \times A_1 \times A_1 \times \dots \times A_1 = A_1$ (a banality, all the characters of A_1 are equal 1). Now let us focus on the excited states of the $3N - 6$ vibrational modes. The excited states may be quite complex, but the most important (and the simplest) are those with all the normal modes in their ground states, except a single mode that is in its first excited state. A transition from the many-oscillator ground state to such an excited state is called a *fundamental transition*. The intensities of the fundamental transitions are by at least one order of magnitude larger than the others. This is why we will focus on the selection rules for such transitions. Let us take one such

singly excited state (with the first mode excited):

$$\psi_1^{\text{osc}} = \psi_{1,1} \psi_{2,0} \psi_{3,0} \cdots \psi_{3N-6,0}. \quad (\text{C.32})$$

The function $\psi_{1,1}$ corresponding to the first excited state transforms according to the irreducible representation Γ , to which the normal mode 1 belongs. Thus, ψ_1^{osc} transforms according to $\Gamma \times A_1 \times A_1 \times A_1 \times \cdots \times A_1 = \Gamma$, i.e. it belongs to the same irreducible representation as $\psi_{1,1}$. Of course, if the only excited mode were the i -th one, then the many-oscillator wavefunction would belong to the same irreducible representation as the wavefunction of the particular oscillator does. We will need this result later.

IR selection rules. Let us consider a molecule with a fixed position in a Cartesian coordinate system. To excite the molecule, IR light (because the separation of the vibrational levels corresponds to the infrared region) is used, which is polarized along the x axis. Theory of electromagnetism says the transition integral⁴² decides the intensity of the absorption

$$\int \psi_0^{\text{osc}} \hat{\mu}_x \psi_1^{\text{osc}} d\tau, \quad (\text{C.33})$$

where $\hat{\mu}_x$ stands for the dipole moment component x . The selection rules establish which integrals of this kind will be zero for symmetry reasons. To this end we need information about the irreducible representations to which ψ_0^{osc} , $\hat{\mu}_x$, ψ_1^{osc} belong.⁴³ Since ψ_0^{osc} transforms according to A_1 , for the integral to survive, the function ψ_1^{osc} has to belong to the same irreducible representation as $\hat{\mu}_x$ (and therefore x itself). We showed above that ψ_1^{osc} belongs to the same irreducible representation to which the normal mode 1 belongs. In other words, the rule is:

SELECTION RULE IN IR

the transition from the ground state is allowed for those normal modes that transform as x , where x is the direction of light polarization, and similarly for light polarization along y and z .

Raman selection rules. The physics of Raman spectra⁴⁴ is different: rather than direct absorption this is light scattering (in the UV-VIS region) on molecules. It turns out, that beside the light the source is emitting, we also detect quanta of energy lower or higher by $h\nu$, where ν is the vibrational frequency of the molecule.

⁴²The integration goes over the coordinates of the nuclei.

⁴³We are going to analyze the direct product of these three representations. If it contains the fully symmetric representation, the integral is not zero.

⁴⁴Chandrasekhar Venkata Raman (1888–1970), Indian physicist, professor at the University of Calcutta and at the Indian Scientific Institute in Bangalore. In 1928 Raman discovered light scattering that is accompanied by a change of frequency (by frequency of the molecular vibrations). Raman received the Nobel prize in 1930 “for his work on the scattering of light and for the discovery of the effect named after him”.

For the Raman scattering to be non-zero, at least one of the following integrals should be non-zero

$$\int \psi_0^{\text{osc}} \hat{\alpha}_{qq'} \psi_1^{\text{osc}} d\tau, \quad (\text{C.34})$$

where $\hat{\alpha}_{qq'}$ with $q, q' = x, y, z$ is a component of the polarizability tensor which transforms as one of the following (cf. eq. (12.40), p. 636): $qq' = x^2, y^2, z^2, xy, xz, yz$ or their linear combinations (this information is available in the tables of characters). Identical reasoning leads to the conclusion that

the normal mode excited in a fundamental transition has to belong to the same irreducible representation as the product qq' .

It remains to be seen to which irreducible representations the normal modes belong. The procedure consists of two stages.

Stage 1. First, the global Cartesian coordinate system is chosen, Fig. C.7. In this system we draw the equilibrium configuration of the molecule, with numbered atoms. A local Cartesian coordinate system is located on each atom with axes parallel to the axes of the global coordinate system. For each atom, we draw the arrows of its displacements along x, y and z , oriented towards the positive values (altogether $3N$ displacements), assuming that the displacements of equivalent atoms have to be the same. When symmetry operations are applied, these displacements transform into themselves⁴⁵ and therefore form a basis set of a (reducible) representation Γ of the symmetry group of the molecule (in its equilibrium position). This representation will be decomposed into the irreducible representations.

Stage 2. The reducible representation describes the genuine (internal) vibrations as well as the six apparent vibrations (three translations and three rotations). The apparent vibrations correspond to those irreducible representations that are associated to x, y, z (translations) and R_x, R_y, R_z (rotations). We know from the corresponding table of characters what the later ones are. Summing up: the reducible representation mentioned above has to be decomposed into irreducible representations. The decomposition yields $\Gamma = a(\Gamma_1)\Gamma_1 + a(\Gamma_2)\Gamma_2 + a(\Gamma_3)\Gamma_3 \dots$. From this decomposition we have to subtract (in order to eliminate the apparent vibrations) all the irreducible representations the x, y, z, R_x, R_y and R_z belong.

After these two stages we are left with the number of the irreducible representations which pertain to the genuine vibrations.⁴⁶ Only after this can we establish the vibrational selection rules according to the procedure used before. All this will be shown by a simple example of the carbonate anion CO_3^{2-} that in its equilibrium configuration corresponds to the D_{3h} symmetry group, Fig. C.7.

⁴⁵For example, a displacement of an atom along x under a symmetry operation turns out to be a displacement of another equivalent atom.

⁴⁶Rather internal motions. Note that some of these genuine vibrations may correspond to rotations of the functional groups in the molecule.

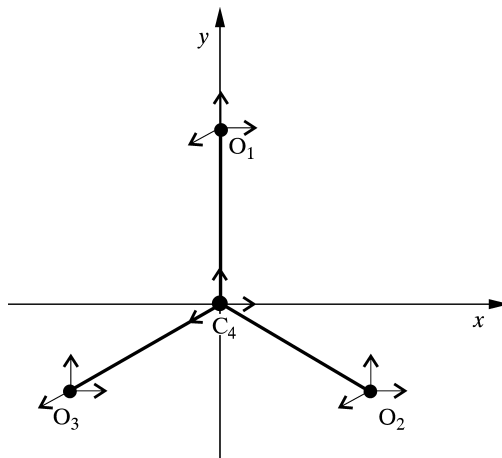


Fig. C.7. The carbonate anion CO_3^{2-} , the coordinate system used and the versors describing the displacements of the atoms.

Example 15. IR and Raman spectra of the carbonate anion. To decompose a reducible representation into irreducible ones, we do not need the reducible representation be given in full details. It is sufficient to know its characters (p. 920). These characters are easy to deduce by considering what happens to the displacement vectors along x_i, y_i, z_i (for atom i) under all the symmetry operations. What will greatly simplify our task is that *only the diagonal* elements of the matrices of the reducible representation contribute to the characters. How it looks in practice is shown in Table C.9.

Thus, the characters of the reducible representation have been found. To decompose the representation, we have to know the table of characters for the D_{3h} symmetry group, Table C.10.

Let us write (in the same order as in Table C.10) the characters of the reducible representation just found:

$$12 \quad 0 \quad -2 \quad 4 \quad -2 \quad 2.$$

Now, let us find (p. 920) how many times $[a(\alpha)]$ the irreducible representation α is present in the reducible representation (the sum over classes: number of operations in class \times the calculated character \times the character of irreducible representation):

$$a(A') = \frac{1}{12} [1 \times 12 \times 1 + 2 \times 0 \times 1 + 3 \times (-2) \times 1 + 1 \times 4 \times 1 + 2 \times (-2) \times 1 + 3 \times 2 \times 1] = 1.$$

Similarly, we find (only needing to know how to multiply such numbers as 1, 2, 3) that

$$a(A) = 1, \quad a(E') = 3, \quad a(A_1'') = 0, \quad a(A_2'') = 2, \quad a(E) = 1.$$

This means that the reducible representation in question decomposes into

$$\Gamma = A'_1 + A'_2 + 3E' + 2A''_2 + E''. \quad (\text{C.35})$$

Table C.9.

Class	The character of the corresponding matrix
E	$\chi(E) = 12$ <i>Justification:</i> each vector transforms into itself. Hence each diagonal element is equal to 1, and the number of them is equal to 3 times the number of atoms = 12
$2C_3$	$\chi(C_3) = 0$ <i>Justification:</i> 0 from the oxygens, because they transform into other oxygens +1(from z_4) + $\cos 120^\circ$ (from x_4) + $\cos 120^\circ$ (from y_4) = 0
$3C_2$	$\chi(C_2) = -2$ <i>Justification:</i> it is sufficient to consider only one of the operations of the class – others will have the same character. Let us take the rotation about the C_2 axis going through O_1 and C. Then the only unit vectors that transform into themselves (eventually changing sign – then the contribution to the character is -1) are those related to O_1 and C. We have $\chi(C_2) = -1$ (from z_4) + (-1) (from z_1) -1 (from x_1) -1 (from x_4) + 1(from y_1) + 1(from y_4) = -2
σ_h	$\chi(\sigma_h) = 4$ <i>Justification:</i> the contribution from each atom will be the same, i.e. χ will be equal to 4 times the contribution from a single atom, the latter equals: -1 (from z) + 1(from x) + 1(from y) = 1
$2S_3$	$\chi(S_3) = -2$ <i>Justification:</i> only C gives a contribution, which is equal to: -1 (from z_4) $-\frac{1}{2}$ (from x_4) $-\frac{1}{2}$ (from y_4) = -2
$3\sigma_v$	$\chi(\sigma_v) = 2$ <i>Justification:</i> Let us take only a single operation from the class, the one, which represents the reflection in the plane going through O_1 and C_4 . Then the contributions to χ are the same for both atoms, and one gives: -1 (from x) + 1(from z) + 1(from y) = 1.

Table C.10. Characters of the irreducible representations of symmetry group D_{3h}

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A'_1	1	1	1	1	1	1		$x^2 + y^2, z^2$
A'_2	1	1	-1	1	1	-1	R_z	
E'	2	-1	0	2	-1	0	x, y	$x^2 - y^2, xy$
A''_1	1	1	1	-1	-1	-1		
A''_2	1	1	-1	-1	-1	1	z	
E''	2	-1	0	-2	1	0	R_x, R_y	xz, yz

From the table of characters, we see that the apparent vibrations (see the irreducible representations corresponding to x, y, z, R_x, R_y, R_z) belong to A''_2, E', A'_2, E'' . After subtracting them from Γ , we obtain the irreducible representations that correspond to the genuine vibrations:

$$A'_1, A''_2, 2E',$$

i.e. one vibration of symmetry A'_1 (and a certain frequency ν_1), two vibrations (each doubly degenerate) of symmetry E' (they differ by frequency $\nu_3 \neq \nu_4$) and one vibration of A''_2 symmetry (corresponding to frequency ν_2).

SELECTION RULES FOR IR:

Therefore, we expect the following selection rules for the fundamental transitions in the IR spectrum for the CO_3^{2-} anion:

1. x and y belong to representation E' , and therefore frequencies ν_3 and ν_4 are active in IR;
2. z belongs to representation A_2'' , and therefore frequency ν_2 is active in IR.

SELECTION RULES FOR RAMAN SPECTRA

For the Raman spectra we expect the following selection rules. The vibrations with the frequency will be active:

1. ν_1 , because $x^2 + y^2$ and z^2 belong to A_1' ;
2. ν_3 and ν_4 , because $x^2 - y^2$ and xy belong to E' ,

while the vibration of the frequency ν_2 will be inactive in Raman spectroscopy, because none of the polarizability components (symbolized by x^2 , y^2 , etc.) belongs to A_2'' .

The results are collected in Table C.11 (sign “+” = active vibration, sign “-” = inactive vibration, the polarization of the light is shown in parentheses).

As seen from Table C.11, in case of the carbonate anion the vibration ν_1 is inactive in IR, but active in Raman spectroscopy, while the opposite is true for ν_2 . The vibrations with frequencies ν_3 and ν_4 are active both in IR and in Raman spectra.

EXCLUSION RULE

If the molecule under study has a centre of symmetry, the *exclusion rule* is valid, i.e. the vibrations that are active in IR are inactive in the Raman spectrum, and *vice versa*.

This follows from the fact that, in this case, x , y , z belong to different irreducible representations than x^2 , y^2 , z^2 , xy , xz , yz . Indeed, the x , y , z are antisymmetric with respect to the inversion operation, whereas x^2 , y^2 , z^2 , xy , xz , yz or their combinations are symmetric with respect to inversion. This guarantees that they belong to *different* irreducible representations, therefore for a molecule with

Table C.11. Transitions in CO_3^{2-} active (+) and inactive (–) in IR and in Raman spectra

Representation	ν	IR (polarization)	Raman
A_1'	ν_1	–	+
A_2''	ν_2	+ (z)	–
E'	ν_3	+ (circular)	+
E'	ν_4	+ (circular)	+

a centre of inversion, the vibrations active in IR are inactive in Raman spectra and *vice versa*.

When do the conclusions drawn from group theory fail?

When deriving the selection rules the following assumptions have been made:

- the molecule is *isolated*,
- elements are represented by *the same isotope*,
- the molecule is in a *stationary state*,
- the vibrations have *small amplitudes*,
- the vibrations are *harmonic*,
- the electromagnetic field interacts with the molecule only through the *electric field-molecule interaction*,
- in the interaction of the molecule with the electromagnetic field only what are called the *dipole transitions* are involved.⁴⁷

However, in practice the molecule is never isolated. In particular, the interactions it undergoes in the liquid or solid state are sufficiently strong to deform the molecule. As a result, we have to do (especially in a liquid) with a population of molecules, each in a different geometry, usually devoid of *any particular symmetry* (for a single molecule this means a non-stationary state), although the molecule is not far away from perfect symmetry (“broken symmetry”).

Suppose for a while that the molecule under consideration *is* indeed isolated. In a substance we usually have several isotopomers, with different distributions of isotopes in the molecules. In most cases this also means broken symmetry. *Broken symmetry means that the selection rules are violated.*

In practice, broken symmetry means that the selection rules cause only a small intensity of forbidden transitions with respect to allowed transitions.

When considering electronic transitions, we assumed that the molecule stays in its equilibrium geometry, often of high symmetry. This may be the most probable configuration,⁴⁸ but the vibrations and rotations deform it. An electronic excitation is fast, and usually takes place with a molecular geometry that differs slightly from the most probable and most symmetric one. This will cause a transition, forbidden for perfectly symmetric geometry, to have a non-negligible intensity.

Deriving the selection rules for IR and Raman spectra, we assumed that the equivalent atoms can differ only by the *sign* of the deviation from the equilibrium position, but its absolute value is the same. This is how it would be for a harmonic

⁴⁷That is, the electric field of the electromagnetic wave within the molecule is assumed to be *homogeneous*. Then the only term in the Hamiltonian related to the light-molecule interaction is $-\hat{\mu}\mathcal{E}$, where $\hat{\mu}$ stands for the dipole moment operator of the molecule and \mathcal{E} is the electric field intensity.

⁴⁸The maximum of the ground-state probability density for the *harmonic* oscillator indeed corresponds to the equilibrium geometry. This is why the selection rules work at all (although in an approximate way).

oscillator. An anharmonicity therefore introduces another reason why a (harmonically) forbidden transition will have non-negligible intensity.

The electromagnetic field has an electric and magnetic component. The selection rules we have derived have not taken into account the presence of the magnetic field. Taking into account the magnetic field introduces some additional selection rules. Also, the wavelength of an electromagnetic wave in the UV-VIS region is of the order of thousands of Å, whereas the length of the molecule is usually of the order of a few Å. This means that the assumption that the electric field of the electromagnetic wave is homogeneous looks good, but in any case the field is not perfectly homogeneous. The deviations will be small, but non-zero. Taking this into account by including further terms besides $-\hat{\mu}\mathcal{E}$, we obtain the interaction of the electric field gradient with the quadrupole moment of the molecule, as well as further terms. This also weakens the selection rules.

Despite these complications, group theory allows for understanding the basic features of molecular spectra. It sometimes works even if the molecule being studied has no symmetry at all, because of a substituent that interferes. Some electronic or vibrational excitations are of a local spatial character and pertain to a portion of the molecule that is (nearly) symmetric. Due to this some optical transitions that are absolutely allowed, because the molecule as a whole does not have any symmetry,⁴⁹ will still have a very low intensity.

⁴⁹But they would be forbidden if the portion in question represented a separate molecule and were symmetric.