

Chemistry 21b – Spectroscopy

Lecture # 8 – Group Theory in Spectroscopy

Molecular symmetry is the unifying thread throughout spectroscopy and molecular structure theory. It makes it possible to classify states, and, more importantly, to determine selection rules without having to do any sophisticated calculations. The application of symmetry arguments to atoms and molecules has its origin in group theory developed by mathematicians in the 19th century, and it is for this reason that the subject is often presented in a rigorous mathematical formulation. However, it is possible to progress quite a long way in understanding molecular symmetry without a detailed mathematical knowledge of the theory of groups, and only a simple introduction to the subject will be outlined below. Besides that in Atkins & Friedman and Harris & Bertolucci, other treatments of molecular symmetry and group theory are given by J.I. Steinfeld, “Molecules and Radiation” (1974), Ch. 6, F. A. Cotton, “Chemical Applications of Group Theory” (1963), and M. Tinkham, “Group Theory and Quantum Mechanics” (1964). The latter book contains a more mathematical discussion for those interested in probing the details of this subject.

The great utility of group theory lies in its abstractness. Provided any set of elements A, B, C, D, \dots obeys the following four conditions, they form a group:

- (1) *Closure*. If A and B are any two members of the group, then their product $A * B$ must also be a member of the group.
- (2) *Associativity*. The rule of combination must be such that the associative law holds. That is, if $A, B,$ and C are any three elements of the group, then $(A * B) * C = A * (B * C)$.
- (3) *Identity*. The group must contain a single element I such that for any element A of the group, $A * I = I * A = A$. I is called the *identity element*.
- (4) *Inverse*. Each element A of the group must have an inverse A^{-1} that is also a member of the group. By the term inverse we mean that $A * A^{-1} = A^{-1} * A = I$, where I is the identity element.

Each molecule has a number of so-called “symmetry elements,” which together comprise the point group to which the molecule belongs (Point groups are so named because of the fact that the symmetry operations in the groups leave at least one point in space unchanged. Space groups leave lines, planes, or polyhedra unchanged, and so are very useful in the crystallographic study of solids.). As Atkins & Friedman describe, for molecules the symmetry operations (in addition to the identity operation) that must be considered include rotation about an axis, reflection about a plane, inversion through a point, or a combination of these operations.

In what follows we’ll take as an example the H_2O molecule. The symmetry elements leave the molecule in an indistinguishable orientation from that before the operation was carried out. This does not mean that the molecule has the exact same orientation, simply that the pattern of equivalent atoms is the same. As Figure 8.1 shows, water has the following symmetry elements:

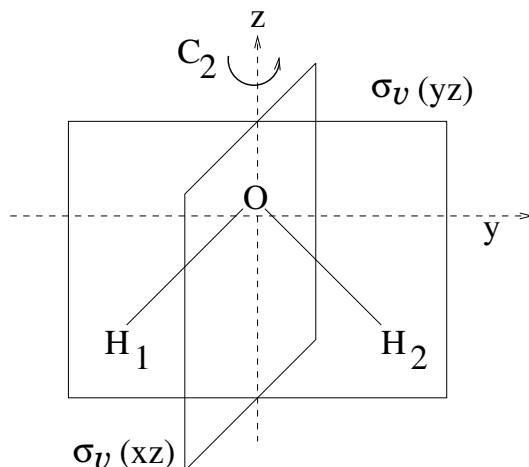


Figure 8.1 An illustration of the various symmetry elements belonging to the C_{2v} group, with water as an illustrative case.

- (i) The “identity” element I : the symmetry operation I consists of doing nothing to the molecule, so that it may seem too trivial to be of importance. However, as noted above it is a necessary element required by the rules of group theory. All molecules have the identity element of symmetry.
- (ii) A “two-fold axis of symmetry” C_2 : rotation of the molecule by $2\pi/n$ radians, with $n=2$, about the z -axis produces a configuration which is indistinguishable from the initial one.
- (iii) a “symmetry plane” $\sigma_v(xz)$ perpendicular to the plane of the molecule: that is, reflection through the plane to an equal distance on the opposite side produces a configuration indistinguishable from the initial one. The subscript ‘ v ’ stands for vertical and implies that the plane is vertical with respect to the highest-fold axis, which is C_2 in this case (Planes that are perpendicular to the highest-fold symmetry axes are called horizontal, or σ_h , planes.).
- (iv) A symmetry plane $\sigma_v(yz)$ in the plane of the molecule. Any planar molecule has at least one plane of symmetry.

A molecule with these 4 particular symmetry elements is said to have C_{2v} symmetry. A useful device for thinking about groups is what is called the multiplication table, which tabulates the products of various pairs of elements within the group. Clearly, the elements of the multiplication table must also be elements in the group. For the C_{2v} group, the multiplication table is as follows:

$$\begin{array}{c}
 \hat{I} \\
 \hat{C}_2 \\
 \hat{\sigma}_v(xz) \\
 \hat{\sigma}_v(yz)
 \end{array}
 \begin{pmatrix}
 \hat{I} & \hat{C}_2 & \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) \\
 \hat{I} & \hat{C}_2 & \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) \\
 \hat{C}_2 & \hat{I} & \hat{\sigma}_v(yz) & \hat{\sigma}_v(xz) \\
 \hat{\sigma}_v(xz) & \hat{\sigma}_v(yz) & \hat{I} & \hat{C}_2 \\
 \hat{\sigma}_v(yz) & \hat{\sigma}_v(xz) & \hat{C}_2 & \hat{I}
 \end{pmatrix}$$

In constructing group multiplication tables, it is helpful to remember that in each row or column of the table each element of the group appears only once. You’ll notice that

certain products in the multiplication table above block-diagonalize into like symmetry elements. These elements are said to be *conjugate*, that is for elements P and Q there is another element X of the group such that $P = X^{-1}QX$. Each group of mutually conjugate elements is called a *class*. For the C_{2v} group each element is in its own class, for the C_{3v} group the C_3 and C_3^2 elements form a class, as do the three vertical reflection planes.

From these tables and a consideration of how the symmetry elements affect various coordinate systems, it is possible to come up with a variety of matrices that multiply in the same way as the symmetry elements do. Any set of non-null square matrices that multiply in the same way as the elements of a group is said to form a *representation* of that group, and the order of the matrices is called the *dimension* of the representation. Not all representations are created equal, that is, some are more useful than others. If the matrices of a representation can be converted by the same similarity transformation into the same block diagonal form, the representation is said to be *reducible*, otherwise the representation is said to be *irreducible*. In quantum theory and spectroscopy, we'll be concerned nearly exclusively with the *irreducible* representations of point groups.

In particular, we'll just state here (for more information consult the books noted above) that in fact the full matrices are often not needed – their traces alone can provide sufficient information. If, in a certain representation, the matrix $\mathbf{D}(\hat{R})$ corresponds to the symmetry operation \hat{R} , then the trace of $\mathbf{D}(\hat{R})$ is called the *character* of \hat{R} for that representation. Tabulations of the characters of the various representations for a group are called, not surprisingly, character tables, and a wide variety of them are presented in the back of Atkins & Friedman. By construction, the classes are listed on the horizontal header of the table, while the irreducible representations are listed on the vertical header to the left. For these irreducible representations and character tables, there are five important theorems that are useful in considering the connection between group theory and spectroscopy:

- (1) The number of non-equivalent irreducible representations of a group is equal to the number of classes in that group.
- (2) The sum of the squares of the dimensions of all the non-equivalent irreducible representations of a group is equal to the order of the group.
- (3) The sum of the squares of the absolute values of the characters in any irreducible representation is equal to the order of the group.
- (4) The characters of two non-equivalent irreducible representations i and j satisfy

$$\sum_{\hat{R}} \chi_i^*(\hat{R})\chi_j(\hat{R}) = 0 \quad (8.1)$$

where $\chi_i(\hat{R})$ and $\chi_j(\hat{R})$ are the characters of the symmetry operation \hat{R} in the representations i and j , and where the sum runs over the h symmetry operations of the group.

- (5) If the characters for some particular representation i satisfy

$$\sum_{\hat{R}} |\chi_i(\hat{R})|^2 = h \quad (8.2)$$

then i is irreducible.

Theorem (4) implies that two non-equivalent irreducible representations cannot have the same set of characters, while (3) and (4) can be combined into the so-called Great Orthogonality Theorem, or

$$\sum_{\hat{R}} \chi_i^*(\hat{R})\chi_j(\hat{R}) = h\delta_{ij} \quad (8.3)$$

which is very useful in putting together character tables. For the C_{2v} group, which is of order 4, there are four symmetry elements and so each of the four irreducible representations must be nondegenerate. For the C_{3v} group, appropriate for symmetric tops like ammonia or acetonitrile, the number of symmetry elements is six (the identity, \hat{C}_3 , \hat{C}_3^2 , and three $\hat{\sigma}_v$ elements). It turns out in this case that there are three irreducible representations, and so

$$l_1^2 + l_2^2 + l_3^2 = 6 \quad (8.4)$$

The only set of three integers which satisfies (8.4) is 1,1,2, and so the C_{3v} group must have two non-degenerate and one doubly degenerate irreducible representations. For the C_{2v} group, the character table is as follows:

Table 8.1 Different “symmetry types” in the character table of the group C_{2v}

\hat{I}	\hat{C}_2	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	Label	
+1	+1	+1	+1	A ₁	z
+1	+1	-1	-1	A ₂	
+1	-1	+1	-1	B ₁	x
+1	-1	-1	+1	B ₂	y

The different irreducible representations, or symmetry types, are given labels: A₁, A₂, B₁, and B₂ in this case. Functions which are symmetric with respect to the principle symmetry axis C_n are always denoted with the letter A, whereas those that are antisymmetric with respect to C_n are denoted with the letter B. The subscripts 1 or 2 then follow from the behavior under the other elements $\sigma_v(xz)$ and $\sigma_v(yz)$. The representation A₁ is called the “totally symmetric” representation, must always be present, and is always listed first in character tables. As they should be, the character sets for each of the representations are orthogonal to each other. Also listed in Table 8.1 are the symmetry types of the (x, y, z) coordinates (or translation operators). We’ll find these to be quite useful in the consideration of selection rules in just a bit.

For groups with irreducible representations that are degenerate, the letter E refers to those that are two dimensional, while three, four, and five dimensional irreducible representations are labeled T, G, H . If a molecule has a center of symmetry (is in CO₂ or SF₆, for example, a subscript g (for *gerade*) or u (for *ungerade*) is added according to whether the character is symmetric or antisymmetric under inversion. By convention, the identity operator is always listed first in the header row of the character table, and

the number within the first column of the character table itself provides you with the dimensionality of the irreducible representation.

Given the abstractness of group theory, why do we care? Consider, for a moment, the electronic and vibrational wave functions of a molecule. Using the Born-Oppenheimer approximation, we know that they must satisfy the Schrödinger equation, or $\hat{H}\psi_{j,v} = E_v\psi_{j,v}$, where \hat{H} , $\psi_{j,v}$, and E_v are either the electronic or vibrational Hamiltonian, wave functions, and energies. The subscript v levels the energy levels and the subscript j distinguishes the wave functions belonging to each level E_v . Thus, if the v th level is n -fold degenerate, $j = 1, 2, \dots, n$. If \hat{O}_R is an operator corresponding to one of the symmetry operations in the point group of a molecule, it can be shown that

$$[\hat{O}_R, \hat{H}] = 0 \quad (8.5)$$

The proof of this is straightforward, but tedious, and so we omit it here. Clearly the potential terms do not change if the molecular framework is altered into one which is undistinguishable from the original, but the kinetic energy operator is also unchanged and so the commutation relation holds (for a full discussion of these points, pp. 117-123 of *Molecular Symmetry* by D.S. Schonland (Van Norstrand, Princeton, 1965) is a good place to start). Thus, we are free to choose our wavefunctions such that they are eigenfunctions not only of the total energy but also of the symmetry operations within the point group. This has two critical implications:

- (1) The wave functions of each electronic or vibrational level of a molecule transform according to an irreducible representation of the molecular point group, and
- (2) The degree of degeneracy of an energy level, barring “accidental degeneracies,” is equal to the dimension of the irreducible representation to which its wavefunction belongs.

Thus, even without solving the Schrödinger equation, we *know* the possible degeneracies at the very start! Every vibrational level of a C_{2v} molecule must be non-degenerate, E levels are doubly degenerate, T levels are triply degenerate, etc. Given the behavior we know must exist under the individual symmetry operations of the group, we also know a great deal about the quantitative behavior of the wavefunctions (number of nodes, symmetry, and so forth). As a simple example, let’s again consider the water molecule, and how its molecular orbitals are assembled.

First we examine the symmetry properties of some atomic orbitals attached to the nuclei, for example, the 1s, 2s, and 2p function on O. What happens to each of these functions if the symmetry operations are applied? Clearly, the 1s and 2s orbitals remain unchanged, as does the 2p_z orbital. However, under some symmetry operations, the 2p_x and 2p_y orbitals are transformed into themselves, but under others, they end up as “-” themselves. These properties are summarized in Table 8.2.

Now consider a 1s orbital attached to each of the hydrogens. Under C_2 and $\sigma_v(xz)$, the 1s orbital on atom #1 is transformed into the 1s orbital on atom #2 and *vice versa*. Thus, these 1s orbitals on hydrogen do not have a definite symmetry type, since they do not transform into + or - themselves. However, the linear combinations 1s(H₁) + 1s(H₂) and 1s(H₁) - 1s(H₂) do have a definite character.

The total wavefunction of the H₂O molecule is built up as the product of a number of one electron orbitals, such as those listed in Table 8.2, each with a definite symmetry type. Thus, the total wave function has a definite symmetry type, and this type can be used as the “label” to characterize the electronic state. For example, the ground state wave function of H₂O is totally symmetric, so that the state can be labelled as \tilde{X}^1A_1 ; the first excited electronic state is the \tilde{A}^1B_1 state (we’ll go over the naming conventions for electronic states later in the course). As we’ll see next time, the vibrational wavefunctions can also be characterized according to their symmetry.

Table 8.2

Function	\hat{I}	\hat{C}_2	$\hat{\sigma}_{xz}$	$\hat{\sigma}_{yz}$	Label
1s(O)	+	+	+	+	A ₁
2s(O)	+	+	+	+	A ₁
2p _z (O)	+	+	+	+	A ₁
2p _x (O)	+	-	+	-	B ₁
2p _y (O)	+	-	-	+	B ₂
1s(H ₁)	+	1s(H ₂)	1s(H ₂)	+	?
1s(H ₂)	+	1s(H ₁)	1s(H ₁)	+	?
1s(H ₁) + 1s(H ₂)	+	+	+	+	A ₁
1s(H ₁) - 1s(H ₂)	+	-	-	+	B ₂

Having classified the electronic or vibrational states of H₂O as definite symmetry types within the C_{2v} point group, we can then use the very powerful theorems of group theory to immediately say whether a certain transition will be, for example, electric dipole allowed or not, without any calculations! The physical reasoning is exactly the same as for the case of the parity selection rule in atoms: the integrand has to be a totally symmetric function, because otherwise integration over the whole coordinate space will give zero. In group-theoretical language: the product of the symmetry types of the wave functions involved and that of the dipole operator – or any other operator such as the magnetic dipole or Raman (polarizability) interactions – must be A₁.

For example, in the case of H₂O, we have to figure out whether the integrand in

$$\langle \tilde{A}^1B_1 | \vec{d} | \tilde{X}^1A_1 \rangle = \int \Psi_{\tilde{A}}^* \vec{d} \Psi_{\tilde{X}} d^3x \quad (8.6)$$

is totally symmetric. One can show that the electric dipole operator $\vec{d}=(x,y,z)$ also has definite symmetry. Just as the 2p-functions, the x-component transforms according to B₁, the y-component according to B₂, and the z-component according to A₁ symmetry. (These are noted in the last column of Table 8.1, and along with terms for rotational and Raman interactions they are listed in the character tables presented in Hollas). Now is where the

character tables become very useful because we can use simple multiplication rules for the symmetry types to find the overall symmetry of the integrand of (8.6):

$$A \otimes A = A; \quad A \otimes B = B; \quad B \otimes B = A; \quad 1 \otimes 1 = 1; \quad 1 \otimes 2 = 2; \quad 2 \otimes 2 = 1 \quad , \quad (12.7)$$

where the symbol \otimes is called the *direct product* in group theoretical language. To calculate direct product for two, or more, representations, all we need do is take the individual products of the characters of the individual symmetry operations and classify the result. There is a short compendium of direct product results for important groups in Appendix 1 of Atkins.

Thus, for the z-component of the dipole operator we obtain:

$$B_1 \otimes A_1 \otimes A_1 = B_1 \otimes A_1 = B_1 \neq A_1, \quad (8.8)$$

so that the $\tilde{A}^1B_1 - \tilde{X}^1A_1$ transition cannot occur by the z-component of the electric dipole moment operator. For the other components, we find

$$\text{x - component : } B_1 \otimes B_1 \otimes A_1 = A_1 \otimes A_1 = A_1 \quad \dots\text{yes!} \quad (8.9)$$

$$\text{y - component : } B_1 \otimes B_2 \otimes A_1 = A_2 \otimes A_1 = A_2 \neq A_1. \quad (8.10)$$

Thus, the transition $\tilde{A}^1B_1 - \tilde{X}^1A_1$ is electric dipole allowed through the x-component of the operator. Similar procedures are used to examine whether vibrational transitions are allowed or forbidden by symmetry, a process we'll look at later this week.

One can show that there are only a handful of possible symmetry groups to which molecules can belong; C_{2v} is certainly one of the most common ones. For each point group, one can label the electronic and/or vibrational states according to their symmetry types or representations. The character tables of the possible representations, and their behavior under the symmetry operations of a certain group, given in the back of the textbooks mentioned above and in Atkins, are therefore extraordinarily useful once you know how to read them. We'll explore next the normal mode approach to molecular vibrations, and in this exploration we'll make great use of group theory in order to simplify the calculations.