SYMMETRY AND BROKEN SYMMETRY IN MOLECULES

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Summary

A molecule has 'symmetry' and symmetry is conventionally exploited in molecular science by using the point group of the molecule. Point group symmetry is based on the shape of a molecule in its equilibrium configuration. By virtue of the fact that molecules can vibrate and rotate, and the electrons in it can orbit, a molecule can exist in many different 'energy states.'

The states of a molecule can be 'symmetry labeled' by using its point group. Such labels are used as an aid in understanding the states of a molecule, and to determine whether a molecule, when it is in a certain energy state, can absorb electromagnetic radiation (light).

This can be done without having to resort to elaborate calculations. For example, it is easy to use symmetry to determine which molecules will become 'greenhouse gases' when present in significant concentrations in the earth's atmosphere, and to understand that ozone protects us by absorbing ultraviolet radiation.

Symmetry can also be used to determine whether a molecule will have optically active enantiomers. However, point group symmetry does have some important limitations and a more fundamental definition of symmetry involves energy invariance.

This leads to the introduction of the molecular symmetry group which can deal with the problems caused by rotational centrifugal distortion and large amplitude internal motions, both of which alter the shape and point group symmetry of a molecule.

The final topic of the article is a tentative probe into the future suggesting that the study of the effects of broken symmetry in molecules may deepen our understanding of the subject. The asymmetry between the amounts of the right and left handed forms of the biological molecules in living organisms, are manifestations of broken symmetry.

1. Introduction

The conventional way we understand molecular symmetry is based on the study of the rotation and reflection symmetry of macroscopic objects such as spheres, tetrahedrons, and triangular prisms. In this article macroscopic objects and their symmetry are discussed first, and then the application of such symmetry ideas to molecules is introduced by focusing on the shape of a molecule when it is held fixed at its equilibrium configuration.

Such considerations lead to an understanding of molecular symmetry that is based on using molecular point groups, and there is a very large literature concerned with using such symmetry groups to solve problems of the electronic and vibrational behavior of molecules. Some examples are given here.

A deeper understanding of symmetry comes about when one realizes that the true origin of molecular symmetry does not involve the shapes of equilibrium structures but rather the invariance of electronic and rotation-vibration energies to certain transformations. This is discussed in Section 5, and among the transformations that are of importance are inversion and identical particle permutation.

This leads to the concept of the molecular symmetry group as a generalization of the molecular point group. It is then possible to develop symmetry groups for the study of molecules that suffer significant distortions caused by rotation or by large amplitude internal contortions. The article ends with a brief discussion of the concept of `broken' symmetry, and a look to the future.

2. The Symmetry of Macroscopic Objects

Consider the solid tetrahedron in Figure 1(a), and the methane (CH_4) molecule in its equilibrium configuration in Figure 2(a). The methane molecule in its equilibrium configuration is tetrahedral

with a proton (i.e., a hydrogen nucleus) at each vertex and a carbon nucleus at the center. Everybody would say that the tetrahedron and the CH_4 molecule are rather symmetrical objects, even though they may not know how to define precisely what is meant by `symmetrical.' It is the purpose of this section to explain how one quantifies the concept of symmetry for a macroscopic object. This will enable us to understand why a tetrahedron is less symmetrical than a sphere but more symmetrical than a

triangular prism. The concepts of rotation and reflection symmetry will be introduced, and we will explain what we mean by a `group' and a `point group.'
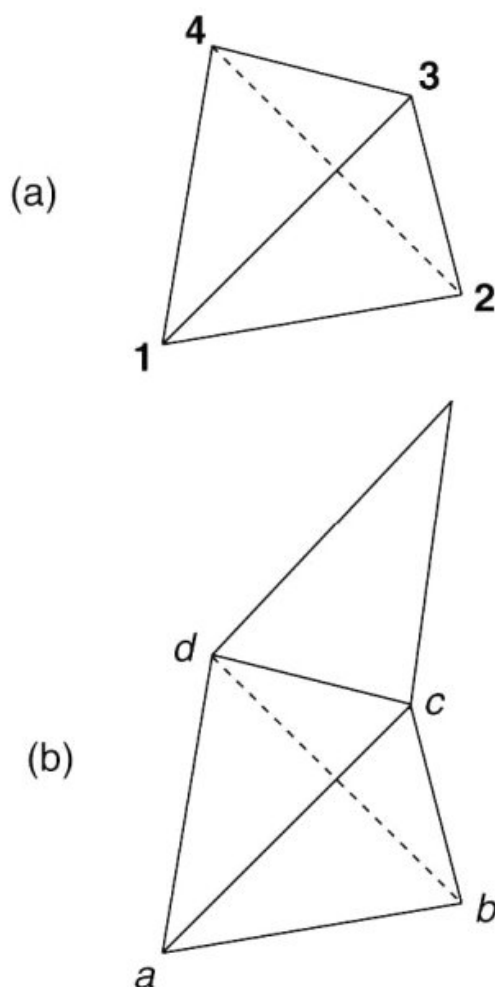

Figure 1: (a) A tetrahedron, and (b) the tetrahedron-box into which the above tetrahedron exactly fits when the lid is closed.
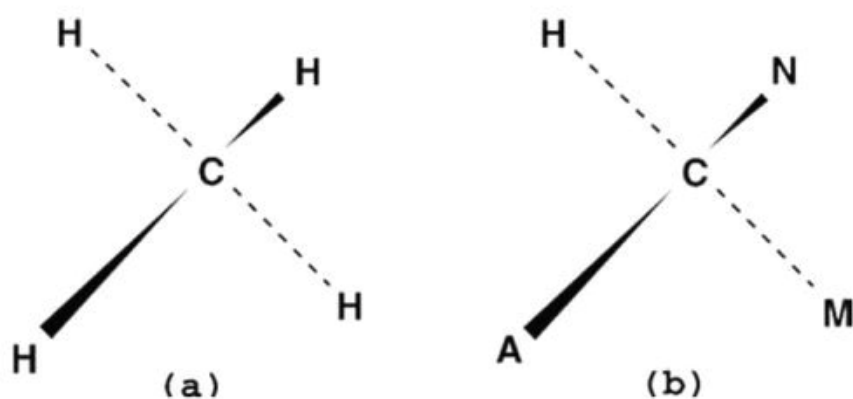

Figure 2: (a) A methane molecule in its equilibrium configuration. The H nuclei are at he vertices of the tetrahedron in Figure 1(a), and the C nucleus is at its center. The H nuclei connected to the C nucleus by 'wedge-shaped' bonds are above the plane of the

paper; those connected by dashed bonds are below the plane. (b) An L-alanine molecule (see Section 4.5 below). The letters M, N, and A represent the substituent groups CH_3, NH_2 and COOH, respectively

For the tetrahedron in Figure 1(a) we label the four vertices 1, 2, 3 and 4. We also imagine a tetrahedron-box as shown in Figure 1(b); it has a hinged face that opens so that the tetrahedron can be exactly fitted in, and we number the four corners of the box *a*, *b, c* and *d*. 'Rotation symmetry' can be understood by determining the number of ways that the tetrahedron can be placed into the tetrahedron-box. We can place vertex 1 into corner `*a*' three different ways depending on which corners of the box we place the vertices 2, 3 and 4. Similarly there are three ways of placing the tetrahedron into the box with vertex 1 at corner '*b*,' three with it at '*c*' and three with it at '*d*.' Thus there are 12 ways of placing the tetrahedron into the tetrahedron-box. This means that there are 12 ways of rotating the tetrahedron about axes passing through its center so that it `looks the same' as it did initially (if we ignore now the numbers on the vertices that make them non-identical). A sphere has more rotational symmetry since there are an infinite number of ways of rotating it so that it looks the same, and an equilateral triangular prism has less rotational symmetry since there are only six ways of rotating it about axes passing through its center so that it looks the same.

The operation of rotating an object from one position to another about an axis that passes through its center so that it looks the same is called a rotation symmetry operation. There are 12 distinct rotation symmetry operations for a tetrahedron, and included in this list is the operation of doing no-rotation called *E* by convention. Each of the rotation symmetry operations involves the rotation of the tetrahedron around an axis, a `rotation symmetry axis,' that passes through the center of the tetrahedron. There are three rotation symmetry axes (that bisect opposite edges of the tetrahedron) about which rotations through 180° are symmetry operations, and four rotational symmetry axes (along each of the CH bonds in Figure 2(a)) about which rotations through 120° or 240° are symmetry operations. Doing any two of the rotation symmetry operations in succession still leads to the tetrahedron looking the same and so the operation of doing two rotational symmetry operations in succession can be represented by a single rotational symmetry operation; this single rotation symmetry operation must be one of the 12 for the tetrahedron (since there are no other). Thus these 12 rotational symmetry operations are closed with respect to the effect of their successive application; no new rotational symmetry operation is introduced. In these circumstances these 12 rotation symmetry operations are said to form a 'group.'(*For a set of elements to form a group it is necessary that the effect of the successive action of any two elements in the set be the same as the effect of another element in the set; one is never sent 'outside' the set by the successive action of any of its elements. Also a group has to contain the 'do-nothing' element E. There are two other requirements that have to be fulfilled for a set of elements to form a group but we do not discuss them here.*) This group is called the rotation symmetry group of a tetrahedron **T**.

In the same way as there are axes passing through the center of the tetrahedron about which there is rotation symmetry there are also planes passing through the center of the tetrahedron across which there is reflection symmetry. For example, a plane passing through the center of the tetrahedron of Figure 1(a) in such a way that it passes through

the vertices numbered 3 and 4 is a reflection plane; after reflecting the two halves of the tetrahedron across the plane it looks the same. There are six reflection planes since there are six ways to chose the two vertices that define the plane. Any two of the reflection symmetry operations done in succession turn out to be equivalent to one of the rotation symmetry operations. Applying a rotation and a reflection symmetry operation in succession we find that sometimes the result is one of the six reflection symmetry operations just described but that we also generate six new operations that are neither one of the 12 rotation symmetry operations nor one of the six reflection symmetry operations; these new operations are called rotation-reflection symmetry operations. The set of 12 rotation symmetry operations, six reflection symmetry operations and six rotation-reflection symmetry operations constitute a group; the effect of the successive application of any two of these 24 operations is equivalent to the effect of one of the 24 elements in the group. All the symmetry elements (rotation axes and reflection planes) pass through the central point of the tetrahedron and as a result the group is called the point group of a tetrahedron. It is given the name $\mathbf{T}_d$. It would be instructive for the reader to draw a tetrahedron with the vertices numbered and then to draw the effects of some of these operations in order to gain familiarity with the concepts. The effect of two symmetry operations in succession could be drawn in order to see with which single symmetry operation this is equivalent.

The point group of a sphere consists of an infinite number of rotation symmetry operations (about an infinite number of rotation symmetry axes that pass through the center of the sphere), and an infinite number of reflection symmetry operations (in an infinite number of reflection planes); it is called $\mathbf{K}_h$. If we only consider the rotation symmetry operations the rotation symmetry group of a sphere is called $\mathbf{K}$. The point group of an equilateral triangular prism consists of six rotation operations (including E), four reflection symmetry operations and two rotation-reflection symmetry operations; it is called $\mathbf{D}_{3h}$.

By determining all the rotation, reflection and rotation-reflection symmetry operations one can determine the point group symmetry of any macroscopic object. There are a finite number of point groups and there are many text books that list them.

3. The Point Group Symmetry of Molecules

The majority of molecules in their ground electronic state have a well defined equilibrium structure. We consider the molecule at equilibrium to be a static classical object rather than what is really is, i.e., a quantum mechanical system of nuclei and electrons in dynamic motion with uncertainties in the particle positions and momenta. In this circumstance we can simply determine the point group symmetry by enumerating the rotation, reflection and rotation-reflection symmetry operations. For example, the equilibrium structure of the water molecule H_2O in its ground electronic state is bent at the oxygen and the OH bond lengths are the same as each other. There are two rotation symmetry operations: E (no-rotation) and C_2 (the operation of rotating the molecule through 180° about the axis that bisects the HOH angle). There are two reflection symmetry operations which we call $\parallel$ (reflection in the molecular plane) and $\perp$ (reflection in the plane perpendicular to the molecular plane and bisecting the HOH angle). The group of these four symmetry operations is called the $\mathbf{C}_{2v}$ point group, and

the water molecule is said to have $\mathbf{C}_{2v}$ point group symmetry. As we have already discussed the equilibrium structure of the methane molecule in its ground electronic state has a tetrahedral shape with the carbon atom at the center and four equal CH bonds. Thus the methane molecule has $\mathbf{T}_d$ point group symmetry.

Examples of some other molecular point group symmetries are:

$\mathbf{C}_s$ the HDO molecule (a monodeuterated water molecule),
$\mathbf{C}_{2h}$ the trans C(HF)C(HF) molecule (*trans*-1,2-difluoroethylene),
$\mathbf{C}_{3v}$ the CH_3F molecule,
$\mathbf{C}_{\infty v}$ the HCN molecule,
$\mathbf{D}_{2d}$ the CH_2CCH_2 molecule (allene),
$\mathbf{D}_{2h}$ the CH_2CH_2 molecule (ethylene),
$\mathbf{D}_{3d}$ the CH_3CH_3 molecule in its `staggered' conformation (ethane),
$\mathbf{D}_{3h}$ the BF_3 molecule,
$\mathbf{D}_{6h}$ the C_6H_6 molecule (benzene),
$\mathbf{D}_{\infty h}$ the CO_2 molecule,
$\mathbf{O}_h$ the SF_6 molecule, and
$\mathbf{I}_h$ the C_{60} molecule (buckminsterfullerene).

In determining these groups we treat the molecule as a classical object that is static at its equilibrium geometry. However, in applications the groups are used to label molecular states (as we discuss below) where these states arise from the quantum mechanical dynamical motion of the electrons and nuclei that constitute the molecule. The criteria used to set up the point group, and the way it is used, seem to be at odds with each other. However, by starting from a different definition of molecular `symmetry,' as we do in Section 5 we will discover what the elements of a point group really are when applied to interpret the quantum mechanical dynamics of a molecule. They do not involve bodily rotations of the molecule, with or without reflection of the complete molecule in a plane, as a naive interpretation suggests. We introduce the name `molecular point group` to distinguish the group having elements with these more subtle properties from the point group of a macroscopic object whose elements have simple geometrical definitions.

4. The Use of Molecular Point Group Symmetry

We use molecular point groups as an aid to help understand the behavior of molecules. To begin it is necessary to determine the symmetry of the vibrational and electronic states, and in this section we summarize how this is done using the water molecule as an example. The phrase `determining the symmetry' means determining the symmetry label (sometimes called symmetry species); each point group comes with a set of symmetry labels and different point groups have a different set of symmetry labels. For example, the $\mathbf{C}_{2v}$ point group of the water molecule has the labels A_1, A_2, B_1 and B_2; the states of the water molecule are therefore of these four symmetry types. For any point group one can find out the symmetry types by looking up its `character table' in a standard text. The character table of the $\mathbf{C}_{2v}$ molecular point group of the water molecule is given in Table 1. For the purpose of understanding which vibrational and electronic states can be excited with the absorption of electromagnetic radiation it is important to know the

symmetry labels for the components of the `dipole moment' μ_α; these are always given in point group character tables (see the μ_α in Table 1).(*Sometimes the notation T_α is used instead of μ_α.*) It is unnecessary to know how these tables have been obtained.

C_{2v}		E	C_2	$\sigma^{\parallel}$	$\sigma^{\perp}$	
A_1		1	1	1	1	μ_x
A_2		1	1	−1	−1	
B_1		1	−1	−1	1	μ_y
B_2		1	−1	1	−1	μ_z

Table 1. The character table of the point group C_{2v}. The *xyz* axis system is shown in Figure 3.

A couple of technical points need to be raised here. We have said that each of the rows of numbers in a character table represents a symmetry label; the technical name for such a symmetry label is an `irreducible representation.' Each of the numbers in an irreducible representation is called a `character' and these numbers can be different from +1 or −1. In general they are the sum of the diagonal elements of a matrix having as dimension the character given under the identity operation E for that irreducible representation. For most point groups there are a finite number of irreducible representations. The C_{2v} group has four irreducible representations and they are all one dimensional with characters +1 or −1. This makes it easy to work with.

Once we have determined the labels on molecular states we are in a position to understand and interpret much of the behavior of the molecule both in isolation, and in the presence of a electromagnetic radiation, without doing any calculations. For example we can use symmetry to determine that water vapor, carbon dioxide and methane can all absorb infrared radiation to become `greenhouse gases' in the earth's atmosphere whereas nitrogen is transparent to infrared radiation allowing global heat to escape. We can also use symmetry to show why ozone absorbs ultraviolet radiation. In the next few paragraphs we will explain how vibrational and electronic states are labeled, and then show how one uses these labels to determine whether a molecule will absorb electromagnetic radiation to undergo transitions between these states. This section will end with a discussion of how symmetry is used to determine whether a molecule is chiral, i.e., whether it has optically active enantiomers. We define 'chiral' and discuss chiral molecules in Section 4.5 below.

4.1. Labeling Vibrational States

Elementary consideration show that water molecules rotate and vibrate and that there are three `normal modes of vibration.' The normal modes of vibration have the symmetry of the `symmetry coordinates' where the symmetry coordinates are linear combinations of bond stretches and angle bends that transform as the irreducible representations of the point group. For example, for water the three symmetry modes are the symmetric OH stretch ($\Delta r_1 + \Delta r_2$), the HOH bend ($\Delta \alpha$), and the antisymmetric OH stretch ($\Delta r_1 − \Delta r_2$). In the symmetric stretching mode the two OH bonds simultaneously stretch and then contract whereas in the antisymmetric mode one OH

bond stretches while the other contracts. Clearly the molecule undergoing the symmetric stretching vibration, or the bending vibration, 'looks the same' after each of the four point group operations; the 'symmetry coordinate' describing the motion is multiplied by +1 by each symmetry operation. Thus each of these two vibrational states has symmetry A_1 in $\mathbf{C}_{2v}$ since the A_1 label has a +1 under each symmetry operation in the character table. However, for the antisymmetric stretching mode (which has one stretched bond and one contracted bond) the symmetry operations C_2 or $\perp$ interchange the long and short bonds so that the symmetry coordinate $(\Delta r_1 - \Delta r_2)$ is multiplied by −1. This vibration is of B_2 symmetry in $\mathbf{C}_{2v}$; the B_2 symmetry label in the character table of the $\mathbf{C}_{2v}$ point group has +1 under the operations E and $\parallel$ and −1 under C_2 and $\perp$. In this way the three symmetry modes transform as irreducible representations of $\mathbf{C}_{2v}$.

A water molecule can be excited to vibrate in several modes at once and the symmetry (or `representation') for such an excited state can be determined from the symmetry of the three normal modes discussed above. For example, if the molecule has one quantum of the antisymmetric stretch and one quantum of the bend simultaneously excited then its symmetry is given by $B_2 \otimes A_1$. To form the product of these two $\mathbf{C}_{2v}$ point group symmetries, we multiply the characters in the A_1 row with those in the B_2 row of Table 1 for each symmetry operation. It is seen that in this way, we obtain the characters of the B_2 row. Thus $B_2 \otimes A_1 = B_2$.

Thus for any molecule once we have the character table of the point group we can determine the symmetry of the normal vibrational modes and the symmetry of any vibrationally excited state.

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Biography Sketches

PHILIP R. BUNKER

Philip Bunker was born in London, England, and read for his Ph.D degree at Cambridge University under the supervision of Professor Christopher Longuet-Higgins. He joined Dr. Gerhard Herzberg's Spectroscopy Group at the National Research Council of Canada as a postdoctoral fellow in 1965, to work with Jon Hougen, and became a staff member in the group the following year. His entire career has been spent at NRC in Ottawa where he is currently a Principal Research Officer in the Theory Group of the Steacie Institute for Molecular Sciences.

He is a theoretical molecular spectroscopist, having written about 160 scientific papers, and is particularly interested in the problems of the dynamics and spectra of molecules having large amplitude internal motions. He is one of the pioneers of the use of nuclear permutation symmetry, and of the development of the molecular symmetry group, for use in solving such problems. Much of his research has been in collaboration with Per Jensen. He has been particularly interested in a special class of molecules that are called quasilinear, and his research in this area lead to the discovery of the infrared spectrum of the methylene free radical, and to the subsequent determination of its precise structure and single-triplet splitting. He has also made fundamental contributions to the study of the breakdown of the Born-Oppenheimer approximation for diatomic and triatomic molecules. Most recently he has been involved with Per Jensen and others in a detailed study of the Renner effect in NH_2^+ and CH_2^+.

In 1988 Philip Bunker was a Fellow of the Japanese Society for the Promotion of Science, and in 1995 he was a Senior Awardee of the Alexander von Humboldt Foundation in Germany. In 1995 he was the Royal Australian Chemical Institute Physical Chemistry Lecturer, and in 1996 he was the Birss Memorial Lecturer at the University of Alberta in Edmonton. He is a past Chair of the International Advisory Committee of the annual Ohio State University International Symposium on Molecular Spectroscopy.

PER JENSEN

Per Jensen was born in Hjørring, Denmark, and received the Danish equivalent of an M.Sc. degree from the University of Århus in 1981 under the supervision of Professor Svend Brodersen. From 1981 to 1983 he worked in Herzberg's Spectroscopy Group at the National Research Council of Canada, first as a NATO Science Fellow and then as an NRC staff member. During the time in Ottawa he did his Ph.D. work under the supervision of P.R.Bunker; he received the Danish Ph.D. degree from the University of

Århus in 1983. Immediately after receiving the Ph.D. degree he was awarded an Alexander von Humboldt fellowship for a 2-year stay at the Physical Chemistry Institute, Justus Liebig University, Giessen, Germany, where he worked in the group of Professor Manfred Winnewisser. After one year at the Department of Chemistry in Arhus he returned to the University of Giessen at the end of 1986 and received the German Habilitation degree there in 1992. Since 1994, he has been the Professor of Theoretical Spectroscopy at the University of Wuppertal, Germany.

His research interests lie in the border area between molecular spectroscopy and quantum chemistry. He develops and applies methods for calculating spectra of small molecules from the underlying properties such as the Born-Oppenheimer potential energy and the dipole moment or, conversely, to determine molecular properties by least-squares fitting of high resolution spectroscopic data. He has authored and coauthored more than 100 articles in the field, making significant contributions to the methods for accurate determination of potential energy surfaces from experimental data, and to the understanding of the anomalous rotation-vibration energy level patterns occurring at high rotational excitation.

Per Jensen won the Franz Vogt Prize of the University of Giessen in 1992, and he was a guest scientist of the Japanese Society for the Promotion of Science in 1997, an IBERDROLA visiting professor at the Consejo Superior de Investigaciones Científicas, Madrid, in 1998, and a Specal Visiting Professor of the Japanese Ministry of Education, Science, and Culture in 2000. He chairs the International Steering Committee for the biennial International Conference on High Resolution Molecular Spectroscopy, and for 1994-1997 he was a member of the International Advisory Committee for the Ohio State University International Symposium on Molecular Spectroscopy.