4.34: The Vibrational and Electronic States of C60

The first step in using Mathcad to do group theory is to enter the character table in matrix form for the symmetry under study. In this example we shall be looking at C_{60} and so the character table for the icosahedral point group has been entered in the matrix C_{Ih} below. The icosahedhral group has 120 symmetry operations which fall into ten classes. Ih is a vector containing the number of symmetry operations in each of the ten classes. Γ_{uma} (unmoved atoms) is a reducible representation showing the behavior of the atoms under the symmetry operations of the icosahedral group.[2] In particular it records the number of atoms that are unmoved by the symmetry operations of the group. Because C_{60} is a cage molecule with no central atom, only the identity operation and the symmetry planes leave atoms unmoved. Obviously the identity operation leaves all sixty carbon atoms unmoved and inspection of the molecule shows that the symmetry planes each contain four atoms which are unmoved by reflection in the plane.

$$
\text{CIh} = \begin{array}{ccccccccccc}
E & C_5 & C_5^2 & C_3 & C_2 & i & S_{10} & S_{10}^3 & S_6 & \sigma \\
\begin{pmatrix}
1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\
3 & \frac{1+\sqrt{5}}{2} & \frac{1-\sqrt{5}}{2} & 0 & -1 & 3 & \frac{1-\sqrt{5}}{2} & \frac{1+\sqrt{5}}{2} & 0 & -1 \\
3 & \frac{1-\sqrt{5}}{2} & \frac{1+\sqrt{5}}{2} & 0 & -1 & 3 & \frac{1+\sqrt{5}}{2} & \frac{1-\sqrt{5}}{2} & 0 & -1 \\
4 & -1 & -1 & 1 & 0 & 4 & -1 & -1 & 1 & 0 \\
5 & 0 & 0 & -1 & 1 & 5 & 0 & 0 & -1 & 1 \\
1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 \\
3 & \frac{1+\sqrt{5}}{2} & \frac{1-\sqrt{5}}{2} & 0 & -1 & -3 & \frac{1-\sqrt{5}}{2} & \frac{1+\sqrt{5}}{2} & 0 & 1 \\
3 & \frac{1-\sqrt{5}}{2} & \frac{1+\sqrt{5}}{2} & 0 & -1 & -3 & -\frac{1-\sqrt{5}}{2} & -\frac{1+\sqrt{5}}{2} & 0 & 1 \\
4 & -1 & -1 & 1 & - & -4 & 1 & 1 & -1 & 0 \\
5 & 0 & 0 & -1 & 1 & -5 & 0 & 0 & 1 & -1
\end{pmatrix}
\end{array}
$$

$Ag : x^2 + y^2 + z^2$
T1g: Rx, Ry, Rz
T2g
Gg
Hg: $2z^2 - x^2 - y^2,\ x^2 - y^2, xy, yz, xz$
Au
T1u: x, y, z
T2u
Gu
Hu

$$
Ih = \begin{pmatrix} 1 \\ 12 \\ 12 \\ 20 \\ 15 \\ 1 \\ 12 \\ 12 \\ 20 \\ 15 \end{pmatrix}
\qquad
\Gamma_{uma} = \begin{pmatrix} 60 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 4 \end{pmatrix}
$$

At this point it is necessary to identify the irreducible representations with a row in the matrix representing the character table for the icosahedral group. It should be noted that these irreducible representations could also have been entered individually as column or row vectors.

$$Ag = \left(CIh^T\right)^{<1>} \quad T1g = \left(CIh^T\right)^{<2>} \quad T2g = \left(CIh^T\right)^{<3>} \quad Gg = \left(CIh^T\right)^{<4>} \quad Hg = \left(CIh^T\right)^{<5>}$$
$$Ag = \left(CIh^T\right)^{<1>}$$
$$Au = \left(CIh^T\right)^{<6>} \quad T1u = \left(CIh^T\right)^{<7>} \quad T2u = \left(CIh^T\right)^{<8>} \quad Gu = \left(CIh^T\right)^{<9>} \quad Hu = \left(CIh^T\right)^{<10>}$$

The order of the group (the normalization constant) is the sum of the total number of symmetry operations.

$$h = \sum Ih \quad h = 120$$

The irreducible representations are a set of orthonormal basis vectors that span the Ih space. This is demonstrated below for several cases.

$$\frac{\sum \overrightarrow{(IhAgAg)}}{h} = 1 \qquad \frac{\sum \overrightarrow{(IhT1gT1g)}}{h} = 1 \qquad \frac{\sum \overrightarrow{(IhAgT1u)}}{h} = 0 \qquad \frac{\sum \overrightarrow{(IhGuHu)}}{h} = 0$$

These vector operations are the symmetry equivalent of the quantum mechanical overlap integrals.

Vibrational Spectroscopy

One of the major goals of a symmetry analysis is to determine how the individual degrees of freedom of the molecule behave under the symmetry operations of the group. This is particularly important in interpreting or predicting the infrared or Raman spectrum of a molecule. The easiest way to find the behavior (reducible representation) of C60's 180 degrees of freedom under the symmetry operations of the Ih group is to take the direct product of Γ_{uma} with the T_{1u} irreducible representation for translation in the x, y, and z directions.[2]

$$\Gamma_{tot} = \overrightarrow{(\Gamma_{uma} T1u)} \quad \Gamma_{tot}^T = (\,180 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 0 \quad 4\,)$$

Now it is possible to find which irreducible representations contribute to Γ_{tot} by calculating the normalized vector sums shown below.[3] The irreducible representations are the unit vectors of Ih space and any other vector in that space can be written as a linear combination of the unit vectors. Taking the product of each irreducible representation with the reducible representation, Γ_{tot}, yields the appropriate coefficient in the linear combination.

$$\frac{\sum \overrightarrow{(IhAg\Gamma_{tot})}}{h} = 2 \quad \frac{\sum \overrightarrow{(IhT1g\Gamma_{tot})}}{h} = 4 \quad \frac{\sum \overrightarrow{(IhAg\Gamma_{tot})}}{h} = 4 \quad \frac{\sum \overrightarrow{(IhGu\Gamma_{tot})}}{h} = 6 \quad \frac{\sum \overrightarrow{(IhHg\Gamma_{tot})}}{h} = 8$$

$$\frac{\sum \overrightarrow{(IhAu\Gamma_{tot})}}{h} = 1 \quad \frac{\sum \overrightarrow{(IhT1u\Gamma_{tot})}}{h} = 5 \quad \frac{\sum \overrightarrow{(IhT2u\Gamma_{tot})}}{h} = 5 \quad \frac{\sum \overrightarrow{(IhGu\Gamma_{tot})}}{h} = 6 \quad \frac{\sum \overrightarrow{(IhHu\Gamma_{tot})}}{h} = 7$$

This result can also be computed more compactly as follows:

$$i = 1..10 \quad X_i = \frac{\sum \left(\overrightarrow{\left[Ih(CIh^T)^{<i>} \Gamma_{tot} \right]} \right)}{h} \quad X^T = (\,2 \quad 4 \quad 4 \quad 6 \quad 8 \quad 1 \quad 5 \quad 5 \quad 6 \quad 7\,)$$

Of the 180 degrees of freedom that C_{60} has, three are due to translation of the center of mass in Cartesian space (T_{1u}) and three are due to rotation about the Cartesian axes (T_{1g}). This leaves 174 vibrational degrees of freedom. They have the following symmetry properties.

$$\Gamma_{vib} = \Gamma_{tot} - T1u - T1g$$

$$i = 1..10 \quad X_i = \frac{\sum \left(\overrightarrow{\left[Ih(CIh^T)^{<i>} \Gamma_{vib} \right]} \right)}{h} \quad X^T = (\,2 \quad 3 \quad 4 \quad 6 \quad 8 \quad 1 \quad 4 \quad 5 \quad 6 \quad 7\,)$$

One important consequence of the high symmetry of C_{60} is that many of the vibrational modes are degenerate. As the result above shows there are only 46 distinct vibrational modes. Another consequence of the symmetry of C_{60} is that most of these modes are not IR or Raman active.[4] In fact only the four T_{1u} vibrational modes are IR active and they appear at 528, 577, 1180, and 1430 cm-[1] with varying intensities. Sample calculations for the transition moment for IR transitions are shown below. Those with transition moments of zero are forbidden.

$$\frac{\sum \overrightarrow{(IhT1gT1uAg)}}{h} = 1 \quad \frac{\sum \overrightarrow{(IhT1uT1uAg)}}{h} = 1 \quad \frac{\sum \overrightarrow{(IhGgT1uAg)}}{h} = 0 \quad \frac{\sum \overrightarrow{(IhHuT1uAg)}}{h} = 0$$

These vector multiplications are the symmetry representations of the quantum mechanical integrals for transition moments. For the transition moment to have a non-zero value, the vector product must span the totally symmetric irreducible representation, Ag. In the examples shown above Ag is the symmetry of the ground vibrational state for all vibrational modes, T_{1u} is the symmetry of the electric dipole operator, and T_{1g}, T_{1u}, G_g, and H_u are the irreducible representations for the vibrational states to be excited by the infrared radiation. As these calculations show, only the T_{1u} vibrational modes have a non-zero transition moment.

However, it is important to realize that the group theoretical analysis given above, and those that follow, can only decide which transitions are forbidden. They do not provide the transition probabilities of the transitions which are not forbidden. For example, the fact that the second vector sum above is 1 says nothing about the intensity of the actual absorption in the infrared, only that the vibrational modes with T_{1u} symmetry are not forbidden.

There are ten Raman active modes, two modes with Ag symmetry and eight with Hg symmetry. They appear at the following frequencies: 273, 436, 496, 710, 773, 1100, 1250, 1435, 1470, and 1570 cm^{-1}.[4] The calculation is similar to that for IR activity

except that the operators for the Raman interaction are the quadratic forms (the components of the polarizability tensor) which transform as Ag and Hg, as shown in the Ih character table.

$$\frac{\sum \overrightarrow{(IhAgAgAg)}}{h} = 1 \qquad \frac{\sum \overrightarrow{(IhT1uAgAg)}}{h} = 0 \qquad \frac{\sum \overrightarrow{(IhT1uHgAg)}}{h} = 0 \qquad \frac{\sum \overrightarrow{(IhHgHgAg)}}{h} = 1$$

In these sample calculations we see the basis for the widely used generalization that for a vibrational mode to be IR active it must have the same symmetry as one of the Cartesian coordinates and to be Raman active it must have the same symmetry as one of the components of the polarizability tensor. We also see quite clearly that for a molecule with a center of inversion there is no overlap between the IR and Raman active vibrational modes. In the appendix it is shown that three of the IR active modes and seven of the Raman active modes are stretching vibrations.

Electronic States of the π Electrons

To a first approximation the bonding in C_{60} might be described as follows: each carbon forms σ bonds to its three neighboring carbon atoms using sp^2 hybridized orbitals with the remaining p orbital on each carbon available for π bonding. It is customary in approximate models to treat the π electrons independently of the σ electrons, just as chemists generally assume that they can treat valence electrons independently of the core electrons. The behavior of the π electrons under the symmetry operations of the icosahedral point group is easy to determine. Because the π orbitals are centered on the carbon atoms and are perpendicular to the sp^2 "plane", they have the same symmetry properties as the carbon atoms.

$$\Gamma\pi = \Gamma_{uma}$$

We now decompose Γ_π into its irreducible representations using the method outlined above.

$$\frac{\sum \overrightarrow{IhAg\Gamma_\pi}}{h} = 1 \qquad \frac{\sum \overrightarrow{IhT1g\Gamma_\pi}}{h} = 1 \qquad \frac{\sum \overrightarrow{IhT2g\Gamma_\pi}}{h} = 1 \qquad \frac{\sum \overrightarrow{IhAg\Gamma_\pi}}{h} = 1 \qquad \frac{\sum \overrightarrow{IhGg\Gamma_\pi}}{h} = 2 \qquad \frac{\sum \overrightarrow{IhHg\Gamma_\pi}}{h} = 3$$

$$\frac{\sum \overrightarrow{IhAu\Gamma_\pi}}{h} = 0 \qquad \frac{\sum \overrightarrow{IhT1u\Gamma_\pi}}{h} = 2 \qquad \frac{\sum \overrightarrow{IhT2u\Gamma_\pi}}{h} = 2 \qquad \frac{\sum \overrightarrow{IhGu\Gamma_\pi}}{h} = 2 \qquad \frac{\sum \overrightarrow{IhHu\Gamma_\pi}}{h} = 2$$

Or calculated more compactly:

$$i = 1..10 \quad X_i = \frac{\sum\left(\overrightarrow{\left[Ih\left(CIh^T\right)^{<i>}\Gamma_{uma}\right]}\right)}{h} \quad X^T$$

$$Gamma_{uma} = Ag + T1g + T2g + 2Gg + 3Hg + 2T1u + 2T2u + 2Gu + 2Hu$$

Just as symmetry arguments cannot predict the actual intensities of allowed infrared or Raman transitions, they also can't predict the energy order of these π electron energy levels. However, group theory combined with a Huckel calculation yields the following order.[5]

$$Ag < T1u < Hg < T2u < Gu < (Gg + Hg) < Hu < T1u < T1g < Hg < T2u < Hu < Gg < Gu < T2g$$

With 60 π electrons to distribute in accordance with the Aufbau and Exclusion Principles, the H_{1u} level is the HOMO, the T_{1u} level is the LUMO, and the T_{1g} level is the LUMO +1. This ordering of the levels is consistent with the basic magnetic and electronic properties of C_{60}. For example, it is diagmagnetic with a completely filled HOMO level and it has a reasonably high electron affinity because of the low lying LUMO. The three-fold orbital degeneracy of the LUMO is consistent with the fact that K_3C_{60} and K_6C_{60} are both known, and K_3C_{60} is paramagnetic while K_6C_{60} is diamagnetic. K_4C_{60} is also known and is diamagnetic due to a Jahn-Teller distortion that splits the T_{1u} level into a lower two-fold degenerate level and a higher singlet level.

Calculation of the transition moments for electronic transitions is similar to that for IR and Raman interactions with electromagnetic radiation. The HOMO ---> LUMO electronic transition in C_{60} involves the following change in electronic structure: H_u^{10} ---> $H_u^9 T_{1u}^1$. The ground state, H_u^{10}, has A_g symmetry as a fully filled level. The transition moment between this state and $H_u^9 T_{1u}^1$ configuration is formulated as shown below because H_u^9 has the same symmetry as H_u^1. Starting at the right Ag is the symmetry of the ground electronic state, T_{1u} is the symmetry of the electric dipole operator, (H_uT_{1u}) represents the symmetry of the manifold of excited electronic states associated with the $H_u^9 T_{1u}^1$ electronic configuration (see appendix), and I_h is, as mentioned earlier, the vector containing the number of symmetry operations in each symmetry class.

$$\frac{\sum \overrightarrow{[Ih(HuT1u)T1uAg]}}{h} = 0$$

Thus the HOMO ---> LUMO electronic transition is formally forbidden. However, the HOMO ----> LUMO+1 is allowed as is shown below. In other words the transition moment for this electronic transition spans the A_g irreducible representation

$$\frac{\sum \overrightarrow{[Ih(HuT1g)T1uAg]}}{h} = 1$$

The ($H_u{}^9 T_{1g}{}^1$) excited state consists of 15 microstates with symmetry T_{1u}, T_{2u}, G_u, and H_u (see appendix). Only the transition to the T_{1u} state is allowed and it occurs at 408 nm.[6] In calculating the transition moment for HOMO --> LUMO electronic transition it has been assumed that there was no change in the vibrational state of the molecule. However, it is possible for forbidden electronic transitions to become weakly allowed through coupling to changes in vibrational state. These are called vibronic transitions and they are allowed if the integral shown below is nonzero.

$$\int \int \Psi ex \Psi vx \mu e \Psi eg \Psi vg \, d\tau e \, d\tau v$$

For example, if the formally forbidden HOMO ---> LUMO electronic transition is accompanied by a vibrational transition of A_u, T_{1u}, T_{2u}, G_u, or H_u symmetry the transition may be allowed (see appendix). The vibronic transition moment would be calculated as follows.

$$\frac{\sum \overrightarrow{[Ih(HuT1u)AuT1uAgAg]}}{h} = 1$$

Here ($H_u T_{1u}$) is the manifold of excited electronic states, A_u is the excited vibrational state, T_{1u} is the electric dipole operator, A_g is the ground electronic state, and A_g is the ground vibrational state.

Thus while formally forbidden, the HOMO ---> LUMO transition is weakly allowed through vibronic coupling. This type of mechanism has been used to interpret the visible spectrum of C_{60} and recent analyses have put the lowest spin-allowed, vibronically assisted HOMO ----> LUMO transition at 620 nm.[6]

As can be seen, Mathcad provides an efficient programming environment for performing symmetry analyses with any of the finite point groups. Once a Mathcad worksheet is prepared for one molecule it serves as a template for all other molecules with that symmetry. The only changes that need to be made are to the vector Γ_{uma} which records how many atoms are unmoved by the symmetry operations of the group. Recently, Greathouse has demonstrated how molecules that belong to the infinite point groups can be analyzed numerically.[7]

Literature Cited:

1. Mathcad is a product of MathSoft Inc., 101 Main Street, Cambridge, MA 02142.
2. Harris, D. C.; Bertolucci, M. D. *Symmetry and Spectroscopy: An Introduction to Vibrational and Electronic Spectroscopy*, Dover Publications, Inc.: New York, 1989; Chater 3, pp. 140-142.
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4. Bethume, D. S.; et. al. *Chem. Phys. Lett.* **1991**, 179, 181-186.
5. Hebard, A. F. *Physics Today* **1992**, *45(11)*, 29.
6. Leach, S.; et, al. *Chem. Phys.* **1992**, *160*, 451-466.
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Appendix

This is a demonstration that the $H_u{}^9 T_{1u}{}^1$ configuration yields the manifold of states, T_{1g}, T_{2g}, G_g, and H_g.

$$i = 1..10 \quad X_i = \frac{\sum \overrightarrow{\left[Ih(CIh^T)^{<i>}(HuT1u)\right]}}{h} \quad X^T = \begin{pmatrix} 0 & 1 & 1 & 1 & 1 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

This is a demonstration that the $H_u{}^9 T_{1g}{}^1$ configuration yields the manifold of states, T_{1u}, T_{2u}, G_u, and H_u.

$$X_i = \frac{\sum \overrightarrow{\left[Ih(CIh^T)^{<i>}(HuT1g)\right]}}{h} \quad X^T = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 1 & 1 & 1 \end{pmatrix}$$

As shown earlier the vibrational modes span all of the irreducible representations. This calculation shows which of those modes provide vibrational coupling for the formally forbidden HOMO ---> LUMO electronic transition.

$$X_i = \frac{\sum \overrightarrow{\left[Ih(HuT1u)\left(CIh^T\right)^{<i>} T1uAgAg \right]}}{h} \quad X^T = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 2 & 3 & 4 \end{pmatrix}$$