Group Theoretical Analysis of the Vibrational and Electronic Spectrum of Benzene

Frank Rioux
CSB|SJU

This tutorial deals with the interpretation of the vibrational and electronic spectra of benzene using group theory.

Analysis of the Vibrational Spectrum

The vibrational analysis uses the method of unmoved atoms (uma). The number of unmoved atoms for each symmetry operation is stored in a vector, Γuma. This is converted into a reducible representation (Γvib) for the vibrational degrees of freedom in several steps as is shown below. Next the irreducible representations that contribute to Γvib is determined.

$D6h := (1\ 2\ 2\ 1\ 3\ 3\ 1\ 2\ 2\ 1\ 3\ 3)$ $D6h := D6h^T$ $h := \sum D6h$ $h = 24$

E	C_6	C_3	C_2	C_2'	C_2''	i	S_3	S_6	σ_h	σ_d	σ_v

$$CD6h := \begin{pmatrix} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 & 1 & 1 & 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 & 1 & -1 & 1 & -1 & -1 & 1 \\ 2 & 1 & -1 & -2 & 0 & 0 & 2 & 1 & -1 & -2 & 0 & 0 \\ 2 & -1 & -1 & 2 & 0 & 0 & 2 & -1 & -1 & 2 & 0 & 0 \\ 1 & 1 & 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 \\ 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 2 & 1 & -1 & -2 & 0 & 0 & -2 & -1 & 1 & 2 & 0 & 0 \\ 2 & -1 & -1 & 2 & 0 & 0 & -2 & 1 & 1 & -2 & 0 & 0 \end{pmatrix}$$

A_{1g}: $x^2 + y^2, z^2$
A_{2g}: Rz
B_{1g}:
B_{2g}:
E_{1g}: (Rx, Ry), (xz, yz)
E_{2g}: $(x^2 - y^2, xy)$
A_{1u}:
A_{2u}: z
B_{1u}:
B_{2u}:
E_{1u}: (x,y)
E_{2u}:

$$\Gamma uma := \begin{pmatrix} 12 \\ 0 \\ 0 \\ 0 \\ 4 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 12 \\ 0 \\ 4 \end{pmatrix}$$

$\Gamma trans := \left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle}$ $\Gamma rot := \left(CD6h^T\right)^{\langle 2 \rangle} + \left(CD6h^T\right)^{\langle 5 \rangle}$ $\Gamma tot := \overrightarrow{(\Gamma uma \cdot \Gamma trans)}$

$\Gamma vib := \Gamma tot - \Gamma trans - \Gamma rot$ $i := 1 .. 12$ $Vib_i := \dfrac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^T\right)^{\langle i \rangle} \cdot \Gamma vib\right]}}{h}$

$$Vib^T = (2\ 1\ 0\ 2\ 1\ 4\ 0\ 1\ 2\ 2\ 3\ 2)$$

$$\Gamma_{vib} = 2A_{1g} + A_{2g} + 2B_{2g} + E_{1g} + 4E_{2g} + A_{2u} + 2B_{1u} + 2B_{2u} + 3E_{1u} + 2E_{2u}$$

The symmetry of the vibrational modes and their IR and Raman activity are given below:

IR active: A_{2u} and $3E_{1u}$. Raman active: $2A_{1g}$, E_{1g}, and $4E_{2g}$.

IR active modes are observed at 675, 1035, 1479, and 3036 cm^{-1}, which is consistent with the above analysis. The Raman spectrum is not as clearly resolved

Analysis of the Electronic Spectrum

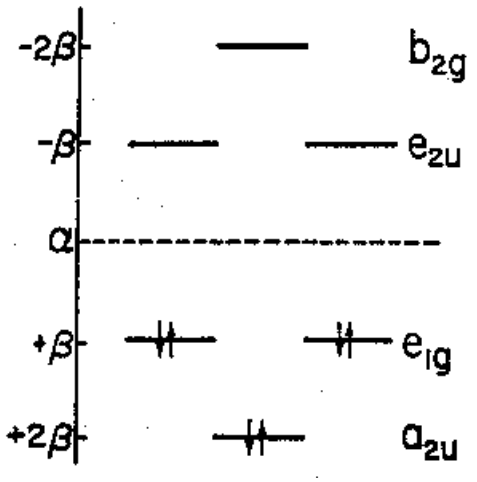
The electronic spectrum to be analyzed (see below) is due to transitions involving benzene's π electrons. The symmetry of the relevant π–electron molecular orbitals is determined by examining how the π orbitals transform under the symmetry operations of the D_{6h} group.

$\Gamma\pi := (6 \;\; 0 \;\; 0 \;\; 0 \;\; -2 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; -6 \;\; 0 \;\; 2)$

$$\Pi_i := \frac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^{T} \right)^{\langle i \rangle} \cdot \Gamma\pi^{T} \right]}}{h}$$

$$\Pi = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 1 \\ 1 \\ 0 \\ 0 \\ 1 \\ 0 \\ 0 \\ 0 \\ 1 \end{pmatrix}$$

A_{1g}: $x^2 + y^2, z^2$
A_{2g}: Rz
B_{1g}:
B_{2g}:
E_{1g}: (Rx, Ry), (xz, yz)
E_{2g}: $(x^2 - y^2, xy)$
A_{1u}:
A_{2u}: z
B_{1u}:
B_{2u}:
E_{1u}: (x,y)
E_{2u}:



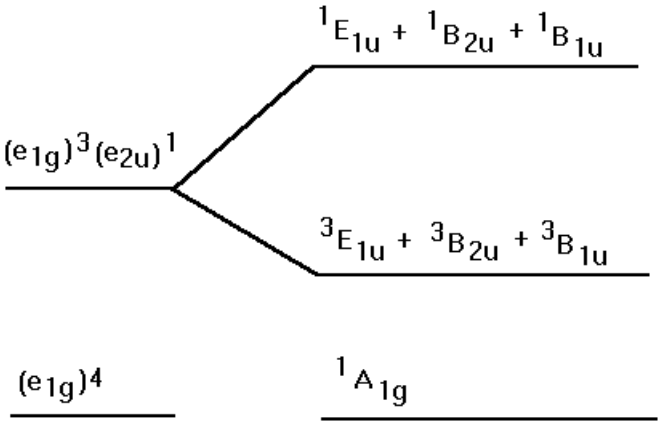
The symmetry of the π-molecular orbitals is $\Gamma\pi = B_{2g} + E_{1g} + A_{2u} + E_{2u}$. The order of the levels from a Huckel calculation is as shown above: A_{2u}, E_{1g}, E_{2u}, and B_{2g}.

The ground electronic state is $A_{2u}(2)$, $E_{1g}(4)$ and has A_{1g} symmetry because the A_{2u} and E_{1g} orbitals are full. The first electronic excited state is $A_{2u}(2)$, $E_{1g}(3)$, $E_{2u}(1)$. This has the symmetry properties of $E_{1g}(1)E_{2u}(1)$ which gives rise to the manifold of states: B_{1u}, B_{2u}, and E_{1u} as is shown below.

$$X_i := \frac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^{T} \right)^{\langle i \rangle} \cdot \left(CD6h^{T} \right)^{\langle 5 \rangle} \cdot \left(CD6h^{T} \right)^{\langle 12 \rangle} \right]}}{h}$$

$X^{T} = (0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 1 \;\; 1 \;\; 1 \;\; 0)$

The electronic energy level diagram consistent with this analysis is shown below. Note that the excited state splits into a set of singlet and triplet exited states. Transitions from the singlet ground state to the triplet excited states are formally forbidden.



For an electronic transition to be allowed the transition moment integral must be greater than zero.

$$\int \Psi_{ex} \cdot \mu_e \cdot \Psi_{eg} \, d\tau_e > 0$$

Only the A_{1g} ---> E_{1u} transition is orbitally allowed as is shown below.

A_{1g} --> B_{1u}

$$\frac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^T\right)^{\langle 9 \rangle} \cdot \left[\left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle}\right] \cdot \left(CD6h^T\right)^{\langle 1 \rangle}\right]}}{h} = 0$$

A_{1g} --> B_{2u}

$$\frac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^T\right)^{\langle 10 \rangle} \cdot \left[\left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle}\right] \cdot \left(CD6h^T\right)^{\langle 1 \rangle}\right]}}{h} = 0$$

A_{1g} ---> E_{1u}

$$\frac{\sum \overrightarrow{\left[D6h \cdot \left(CD6h^T\right)^{\langle 11 \rangle} \cdot \left[\left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle}\right] \cdot \left(CD6h^T\right)^{\langle 1 \rangle}\right]}}{h} = 1$$

Electronic transitions that are orbitally forbidden can occur if they are properly coupled to vibrational transitions. This occurs when the following integral is non-zero. These are called vibronic or vibrationally assisted electronic transitions.

$$\int \int \Psi_{ex} \cdot \Psi_{vx} \cdot \mu_e \cdot \Psi_{eg} \cdot \Psi_{vg} \, d\tau_e \, d\tau_v$$

The orbitally forbidden A_{1g} --> B_{1u} is vibronically assisted by B_{2g} or E_{2g} vibrations.

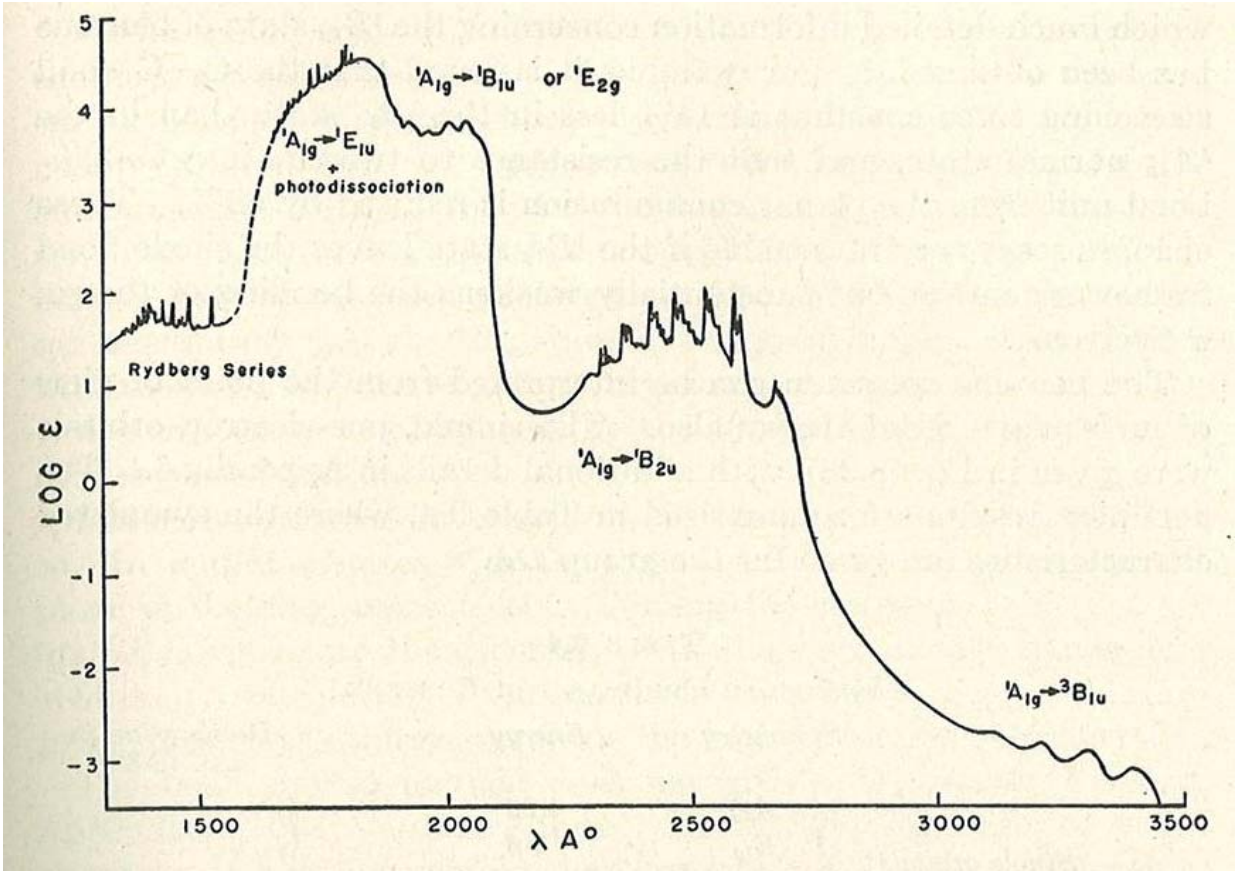
$$X_i := \frac{\overrightarrow{\sum \left[D6h \cdot \left(CD6h^T\right)^{\langle 9 \rangle} \cdot \left(CD6h^T\right)^{\langle i \rangle} \cdot \left[\left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle} \right] \cdot \left(CD6h^T\right)^{\langle 1 \rangle} \cdot \left(CD6h^T\right)^{\langle 1 \rangle} \right]}}{h}$$

$$X^T = (0 \;\; 0 \;\; 0 \;\; 1 \;\; 0 \;\; 1 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0)$$

The orbitally forbidden A_{1g} --> B_{2u} is vibronically assisted by B_{1g} or E_{2g} vibrations. However there is no B_{1g} vibration.

$$X_i := \frac{\overrightarrow{\sum \left[D6h \cdot \left(CD6h^T\right)^{\langle 10 \rangle} \cdot \left(CD6h^T\right)^{\langle i \rangle} \cdot \left[\left(CD6h^T\right)^{\langle 8 \rangle} + \left(CD6h^T\right)^{\langle 11 \rangle} \right] \cdot \left(CD6h^T\right)^{\langle 1 \rangle} \cdot \left(CD6h^T\right)^{\langle 1 \rangle} \right]}}{h}$$

$$X^T = (0 \;\; 0 \;\; 1 \;\; 0 \;\; 0 \;\; 1 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0 \;\; 0)$$



The fully allowed A_{1g} ---> E_{1u} transition is assigned to the most intense transition which occurs at 180 nm. The vibronically assisted A_{1g} --> B_{1u} and A_{1g} --> B_{2u} transitions are assigned to the less intense bands at 200 and 260 nm, respectively. The spin-forbidden $^1A_{1g}$ --> $^3B_{1u}$ is assigned to the lowest energy and lowest intensity transition at 340 nm.