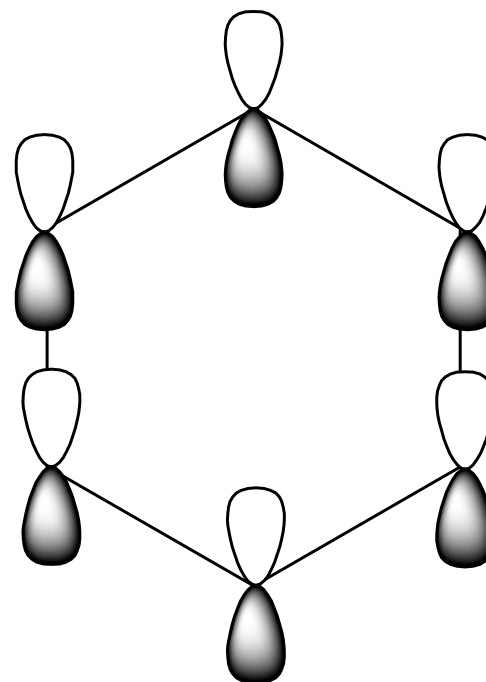# Benzene

Most of the spectroscopy and reactivity of benzene is attributable to its π system. To a good approximation the σ and π orbitals can be separated.

We consider how the 6 p-orbitals transform under D_{6h} symmetry.

In this case we do not need to construct SALCs since there is only one type of orbital.

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	$*_h$	$3*_v$	$3*_d$	Irreps
Γ	6	0	0	0	-2	0	0	0	0	-6	2	0	$a_{2u}+b_{2g}+$ $e_{1g}+e_{2u}$

D$_{6h}$ character table

	E	2C$_6$	2C$_3$	C$_2$	3C'$_2$	3C''$_2$	i	2S$_3$	2S$_6$	σ$_h$	3σ$_d$	3σ$_v$	Linear	Quad
A$_{1g}$	1	1	1	1	1	1	1	1	1	1	1	1		x^2+y^2, z^2
A$_{2g}$	1	1	1	1	-1	-1	1	1	1	1	-1	-1	R$_z$	
B$_{1g}$	1	-1	1	-1	1	-1	1	-1	1	-1	1	-1		
B$_{2g}$	1	-1	1	-1	-1	1	1	-1	1	-1	-1	1		
E$_{1g}$	2	1	-1	-2	0	0	2	1	-1	-2	0	0	(R$_x$, R$_y$)	(xz, yz)
E$_{2g}$	2	-1	-1	2	0	0	2	-1	-1	2	0	0		(x^2-y^2, xy)
A$_{1u}$	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1		
A$_{2u}$	1	1	1	1	-1	-1	-1	-1	-1	-1	1	1	z	
B$_{1u}$	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1		
B$_{2u}$	1	-1	1	-1	-1	1	-1	1	-1	1	1	-1		
E$_{1u}$	2	1	-1	-2	0	0	-2	-1	1	2	0	0	(x, y)	
E$_{2u}$	2	-1	-1	2	0	0	-2	1	1	-2	0	0		

Benzene: reducible representation

	E	2C$_6$	2C$_3$	C$_2$	3C'$_2$	3C''$_2$	i	2S$_3$	2S$_6$	σ$_h$	3σ$_d$	3σ$_v$
G$_p$	6	0	0	0	-2	0	0	0	0	-6	0	2

Decomposition into irreps

$$\Gamma_{\pi} = b_{2g} + e_{1g} + a_{2u} + e_{2u}$$

1. Use projection operator to generate SALCs
2. Normalize the SALCs
3. Set up a secular determinant using the Huckel method
4. Determine energy eigenvalues and total π-energy

$$a_{1g} = \frac{1}{24}\{(1)(1)(6) + (3)(1)(-2) + (1)(1)(-6) + (3)(1)(2)\} = 0$$

$$a_{2g} = \frac{1}{24}\{(1)(1)(6) + (3)(-1)(-2) + (1)(1)(-6) + (3)(-1)(2)\} = 0$$

$$b_{1g} = \frac{1}{24}\{(1)(1)(6) + (3)(1)(-2) + (1)(-1)(-6) + (3)(-1)(2)\} = 0$$

$$b_{2g} = \frac{1}{24}\{(1)(1)(6) + (3)(-1)(-2) + (1)(-1)(-6) + (3)(1)(2)\} = 1$$

$$e_{1g} = \frac{1}{24}\{(1)(2)(6) + (3)(0)(-2) + (1)(-2)(-6) + (3)(0)(2)\} = 1$$

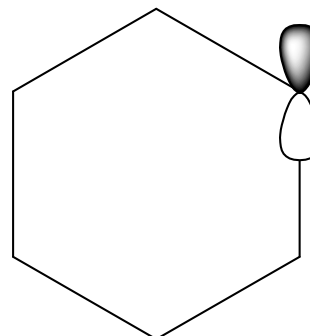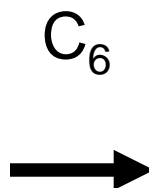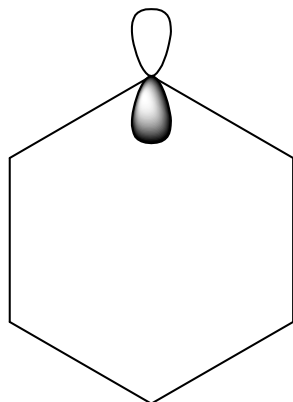$$e_{2g} = \frac{1}{24}\{(1)(2)(6) + (3)(0)(-2) + (1)(2)(-6) + (3)(0)(2)\} = 0$$

$$a_{1u} = \frac{1}{24}\{(1)(1)(6) + (3)(1)(-2) + (1)(-1)(-6) + (3)(-1)(2)\} = 0$$

$$a_{2u} = \frac{1}{24}\{(1)(1)(6) + (3)(-1)(-2) + (1)(-1)(-6) + (3)(1)(2)\} = 1$$

$$b_{1u} = \frac{1}{24}\{(1)(1)(6) + (3)(1)(-2) + (1)(1)(-6) + (3)(1)(2)\} = 0$$

$$b_{2u} = \frac{1}{24}\{(1)(1)(6) + (3)(-1)(-2) + (1)(1)(-6) + (3)(-1)(2)\} = 0$$

$$e_{1u} = \frac{1}{24}\{(1)(2)(6) + (3)(0)(-2) + (1)(2)(-6) + (3)(0)(2)\} = 0$$

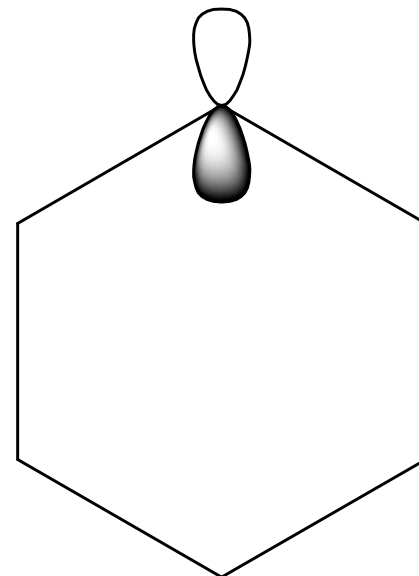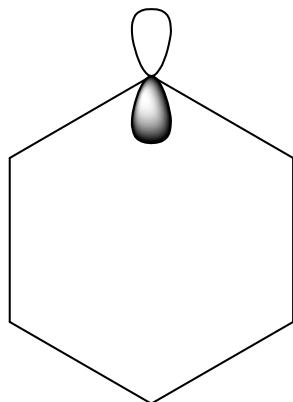$$e_{2u} = \frac{1}{24}\{(1)(2)(6) + (3)(0)(-2) + (1)(-2)(-6) + (3)(0)(2)\} = 1$$

Projection operator approach

The operation required to carry the reference p1 orbital into any of the others.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
1	E	1	1	2	2
2	C_6	1	-1	1	-1
3	C_3	1	1	-1	-1
4	C_2	1	-1	-2	2
5	C_3	1	1	-1	-1
6	C_6	1	-1	1	-1

b_{2g}

C_6
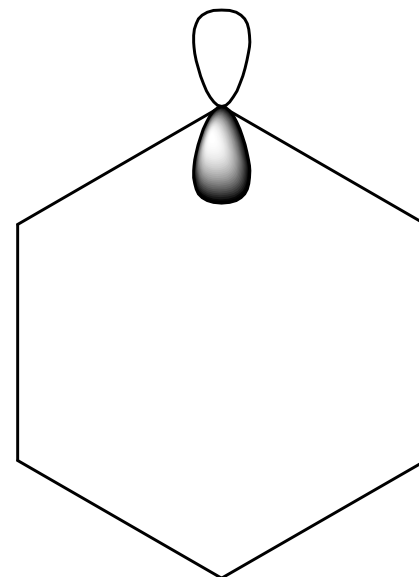
Projection operator approach

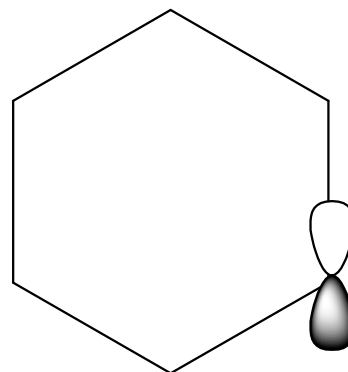The operation required to carry the reference p1 orbital into any of the others.

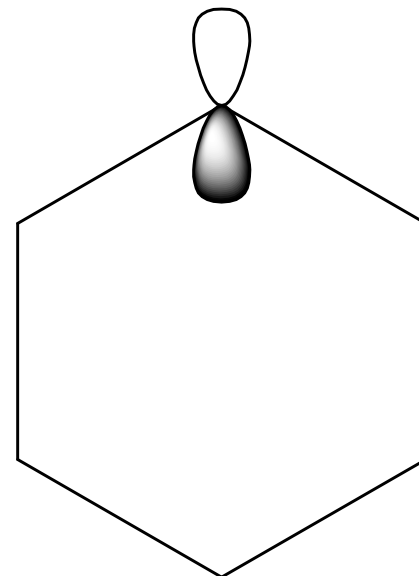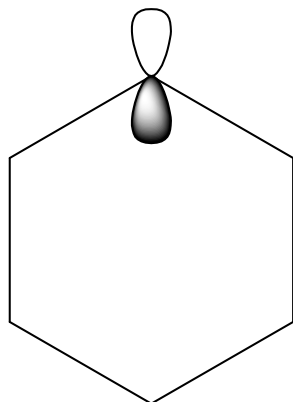| Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
1	E	1	1	2	2
2	C_6	1	-1	1	-1
3	C_3	1	1	-1	-1
4	C_2	1	-1	-2	2
5	C_3	1	1	-1	-1
6	C_6	1	-1	1	-1

b_{2g}

C_3

Projection operator approach

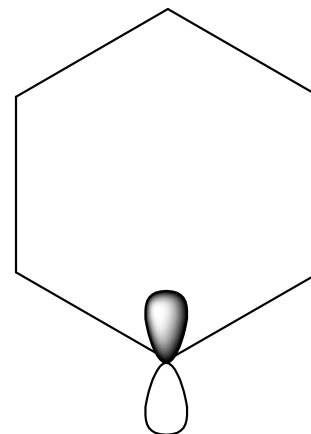The operation required to carry the reference p1 orbital into any of the others.

Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
1	E	1	1	2	2
2	C_6	1	-1	1	-1
3	C_3	1	1	-1	-1
4	C_2	1	-1	-2	2
5	C_3	1	1	-1	-1
6	C_6	1	-1	1	-1

b_{2g}

C_2

MOs using projection operator method

$$\Psi_{b_{2g}} = \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)$$

$$\Psi_{e_{2u}} = \frac{1}{\sqrt{12}}(2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6)$$

$$\Psi_{e_{1g}} = \frac{1}{\sqrt{12}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)$$

$$\Psi_{a_{2u}} = \frac{1}{\sqrt{6}}(p_1 + p_2 + p_3 + p_4 + p_5 + p_6)$$

Using normalization and orthogonalty we obtain

$$\Psi_{e'_{1g}} = \frac{1}{2}(p_2 + p_3 - p_5 - p_6)$$

$$\Psi_{e'_{2u}} = \frac{1}{2}(p_2 - p_3 + p_5 - p_6)$$

$$E_{a_{2u}} = \int \Psi_{a_{2u}} H \Psi_{a_{2u}} d\tau$$

$$\frac{1}{6} \int (p_1 + p_2 + p_3 + p_4 + p_5 + p_6) H (p_1 + p_2 + p_3 + p_4 + p_5 + p_6) d\tau =$$

$$\frac{1}{6} \int p_1 H p_1 d\tau + \frac{1}{6} \int p_2 H p_2 d\tau + \frac{1}{6} \int p_3 H p_3 d\tau + \frac{1}{6} \int p_4 H p_4 d\tau$$

$$+ \frac{1}{6} \int p_5 H p_5 d\tau + \frac{1}{6} \int p_6 H p_6 d\tau + \frac{1}{3} \int p_1 H p_2 d\tau + \frac{1}{3} \int p_2 H p_3 d\tau$$

$$+ \frac{1}{3} \int p_3 H p_4 d\tau + \frac{1}{3} \int p_4 H p_5 d\tau + \frac{1}{6} \int p_5 H p_6 d\tau + \frac{1}{3} \int p_6 H p_1 d\tau$$

$$= \alpha + 2\beta$$

$$E_{b_{2g}} = \int \Psi_{b_{2g}} H \Psi_{b_{2g}} d\tau$$

$$\frac{1}{6} \int (p_1 - p_2 + p_3 - p_4 + p_5 - p_6) H(p_1 - p_2 + p_3 - p_4 + p_5 - p_6) d\tau =$$

$$\frac{1}{6} \int p_1 H p_1 d\tau + \frac{1}{6} \int p_2 H p_2 d\tau + \frac{1}{6} \int p_3 H p_3 d\tau + \frac{1}{6} \int p_4 H p_4 d\tau$$

$$+ \frac{1}{6} \int p_5 H p_5 d\tau + \frac{1}{6} \int p_6 H p_6 d\tau - \frac{1}{3} \int p_1 H p_2 d\tau - \frac{1}{3} \int p_2 H p_3 d\tau$$

$$- \frac{1}{3} \int p_3 H p_4 d\tau - \frac{1}{3} \int p_4 H p_5 d\tau - \frac{1}{6} \int p_5 H p_6 d\tau - \frac{1}{3} \int p_6 H p_1 d\tau$$

$$= \alpha - 2\beta$$

$$H_{11,e_{1g}} = \int \Psi_{e_{1g}} H \Psi_{e_{1g}} d\tau$$

$$\frac{1}{12} \int (2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6) H (2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6) d\tau =$$

$$\frac{1}{3} \int p_1 H p_1 d\tau + \frac{1}{12} \int p_2 H p_2 d\tau + \frac{1}{12} \int p_3 H p_3 d\tau + \frac{1}{3} \int p_4 H p_4 d\tau$$

$$+ \frac{1}{12} \int p_5 H p_5 d\tau + \frac{1}{12} \int p_6 H p_6 d\tau + \frac{1}{3} \int p_1 H p_2 d\tau - \frac{1}{6} \int p_2 H p_3 d\tau$$

$$+ \frac{1}{3} \int p_3 H p_4 d\tau + \frac{1}{3} \int p_4 H p_5 d\tau - \frac{1}{6} \int p_5 H p_6 d\tau + \frac{1}{3} \int p_6 H p_1 d\tau$$

$$= \alpha + \beta$$

$$H_{e_{2u}} = \int \Psi_{e_{2u}} H \Psi_{e_{2u}} d\tau$$

$$\frac{1}{12} \int (2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6) H (2p_1 - p_2 - p_3 + 2p_4 - p_5 - p_6) d\tau =$$

$$\frac{1}{3} \int p_1 H p_1 d\tau + \frac{1}{12} \int p_2 H p_2 d\tau + \frac{1}{12} \int p_3 H p_3 d\tau + \frac{1}{3} \int p_4 H p_4 d\tau$$

$$+ \frac{1}{12} \int p_5 H p_5 d\tau + \frac{1}{12} \int p_6 H p_6 d\tau - \frac{1}{3} \int p_1 H p_2 d\tau + \frac{1}{6} \int p_2 H p_3 d\tau$$

$$- \frac{1}{3} \int p_3 H p_4 d\tau - \frac{1}{3} \int p_4 H p_5 d\tau + \frac{1}{6} \int p_5 H p_6 d\tau - \frac{1}{3} \int p_6 H p_1 d\tau$$
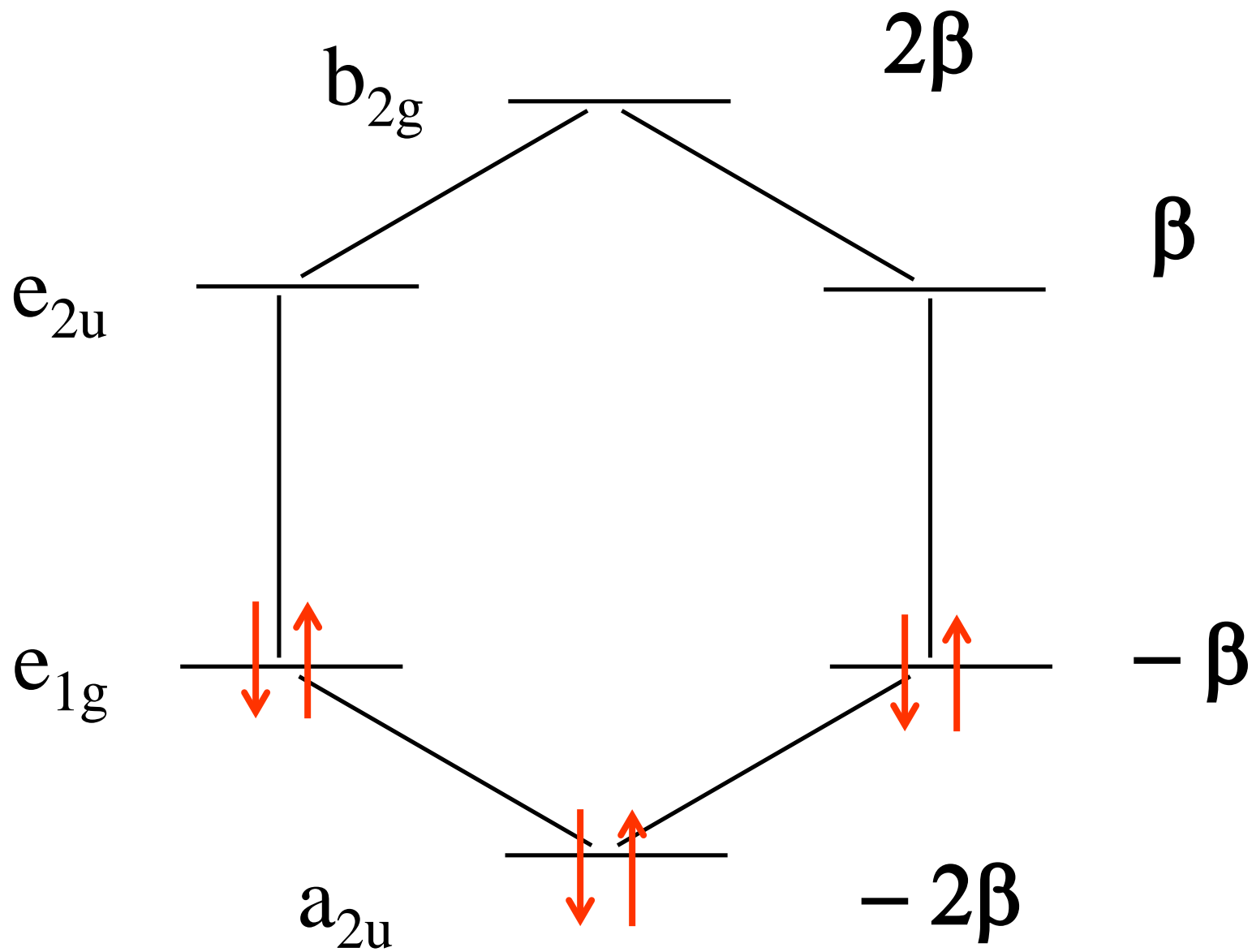
$$= \alpha - \beta$$

Binding energy of π-system
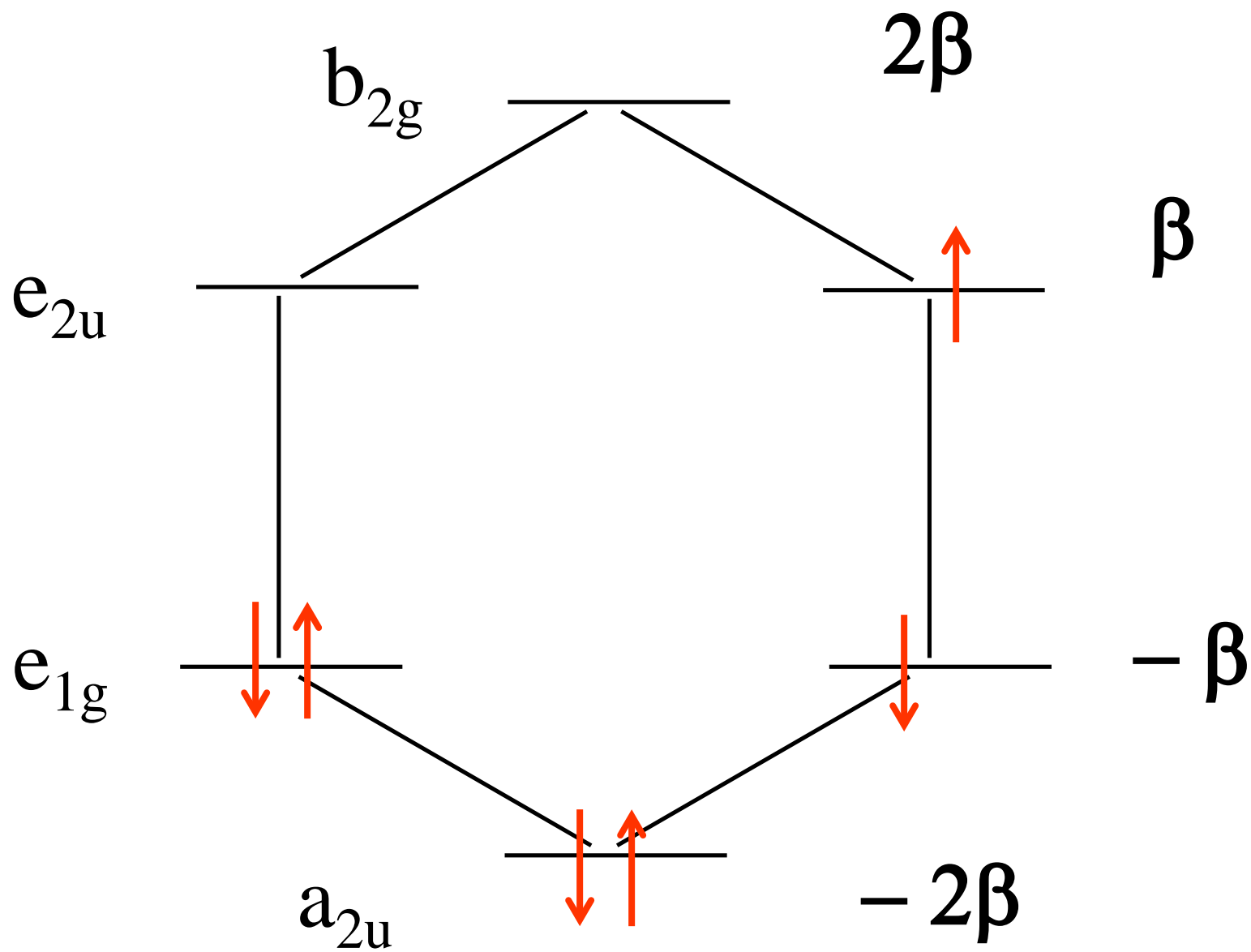
We can calculate the total (π-system) binding energy using the equation:
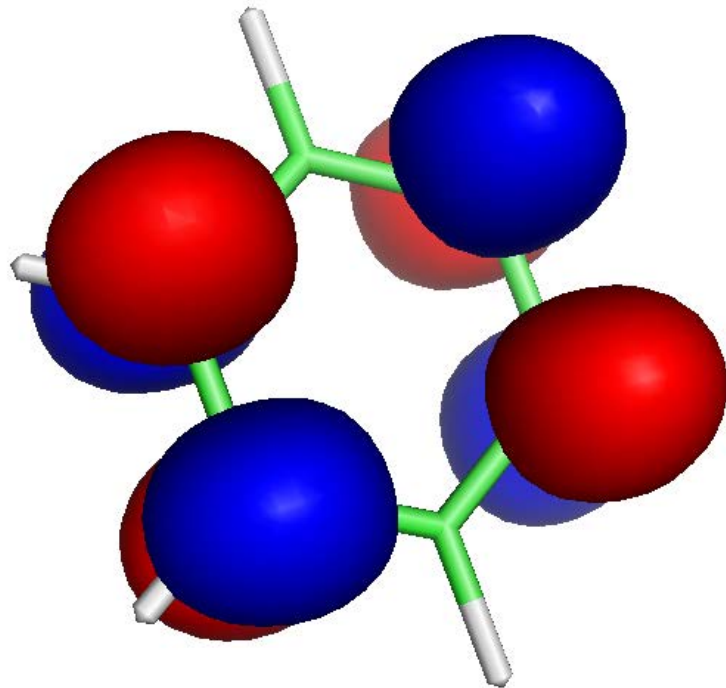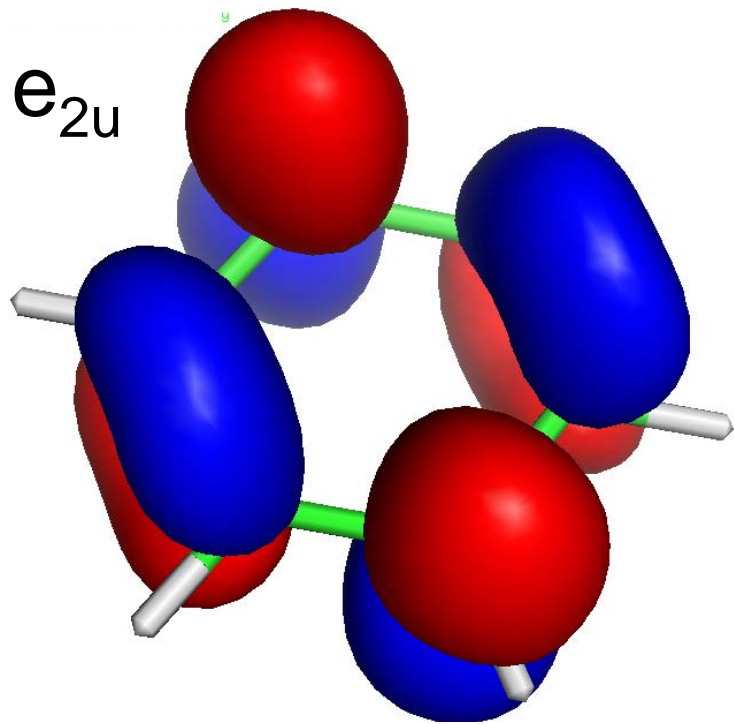
$$E_{\text{binding}} = \sum_{k=1}^{N_{occ}} n_k E_k$$

$$E_{\text{binding}} = 2(-2\,\beta) + 4(-\,\beta) = -8\,\beta$$

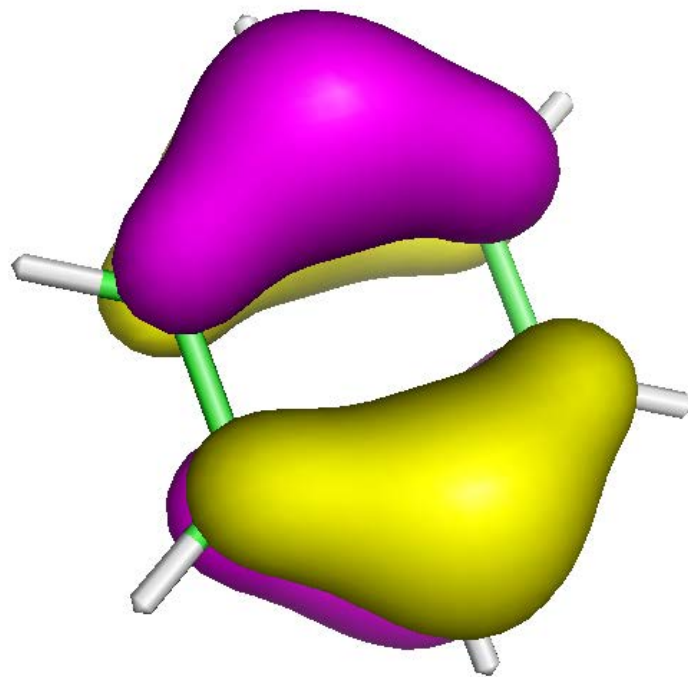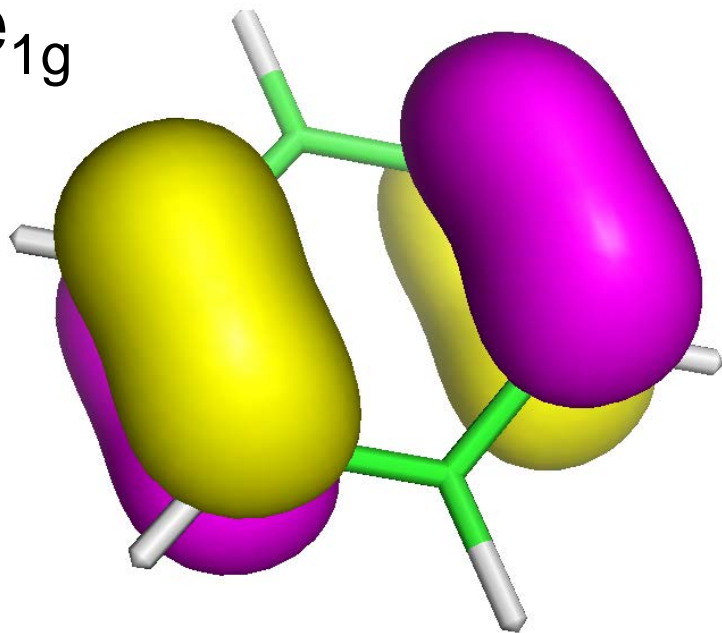This value is more than β more stable than hexatriene.

e_{2u}

e_{1g}

Benzene transitions

In benzene both the HOMO and LUMO are doubly degenerate. This is a common pattern observed in all aromatic molecules. The allowed transitions will have

$$\Gamma_{homo} \otimes \Gamma_{x,y \text{ or } z} \otimes \Gamma_{lumo} = A_{1g}$$

Since it can be tedious to perform separate calculations for x, y and z, we can also use the shortcut:

$$\Gamma_{homo} \otimes \Gamma_{lumo} = \Gamma_{x,y \text{ or } z}$$

MO	Irrep	eV	Occupation
7	a_{1g}	-21.136	2.000
8	e_{1u}	-18.361	2.000
10	e_{2g}	-14.759	2.000
12	a_{1g}	-12.839	2.000
13	b_{1u}	-11.145	2.000
14	b_{2u}	-10.844	2.000
15	e_{1u}	-10.189	2.000
17	a_{2u}	-8.946	2.000
18	e_{2g}	-8.204	2.000
20	e_{1g}	-6.231	2.000
22	e_{2u}	-1.065	0.000
24	a_{1g}	1.500	0.000
25	e_{1u}	2.857	0.000
27	b_{2g}	2.927	0.000
28	e_{2g}	4.039	0.000

Direct product of HOMO-LUMO transition

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
E_{1g}	2	1	-1	-2	0	0	2	1	-1	-2	0	0
E_{2u}	2	-1	-1	2	0	0	-2	1	1	-2	0	0
Γ	4	-1	1	-4	0	0	-4	1	-1	4	0	0

The transition will be allowed if the direct product of the HOMO and LUMO contains one of the irreps corresponding to x, y or z.

$$\Gamma = b_{1u} + b_{2u} + e_{1u}$$

Since e_{1u} transforms as x,y, this transition is an allowed transition. Benzene is a planar absorber meaning that the absorbance is equal along the x and y directions. However, the fact that the irreps also include b_{1u} and b_{2u} means that this transition can also be vibronically allowed.

Vibronically allowed transitions

For benzene we see that there are allowed transitions from the HOMO (e_{1g}) to LUMO (e_{2u}). However, if the symmetry of the molecule is lowered by vibration along an appropriate symmetry normal mode then transitions are also possible:

$$\Gamma_{homo} \otimes \Gamma_{vib} \otimes \Gamma_{x,y \text{ or } z} \otimes \Gamma_{lumo} = A_{1g}$$

Our analysis shows that the $e_{1g} \rightarrow e_{2u}$ transition of benzene spans the irreps b_{1u} and b_{2u}.Transitions with these symmetries would normally be forbidden, but may be allowed by vibronic mixing. How do we identify the mode that may couple these states. When there are many direct products to compute it can be handy to use a product table. The next slide shows the D_{6h} product table. We search for the condition $\Gamma_{homo} \otimes \Gamma_{vib} \otimes \Gamma_{lumo} = \Gamma_{x,y \text{ or } z}$.

Product table for the D_{6h} point group

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_{1u}	E_{2u}
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_{2u}	E_{1u}
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_{2u}	E_{1u}
E_{1g}	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$	E_{1u}	E_{1u}	E_{2u}	E_{2u}	$A_{1u}+A_{2u}+E_{2u}$	$B_{1u}+B_{2u}+E_{1u}$
E_{2g}	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$	E_{2u}	E_{2u}	E_{1u}	E_{1u}	$B_{1u}+B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+E_{2u}$
A_{1u}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_{1u}	E_{2u}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_{1g}	E_{2g}
A_{2u}	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_{1u}	E_{2u}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_{1g}	E_{2g}
B_{1u}	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_{2u}	E_{1u}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_{2g}	E_{1g}
B_{2u}	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_{2u}	E_{1u}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_{2g}	E_{1g}
E_{1u}	E_{1u}	E_{1u}	E_{2u}	E_{2u}	$A_{1u}+A_{2u}+E_{2u}$	$B_{1u}+B_{2u}+E_{1u}$	E_{1g}	E_{1g}	E_{2g}	E_{2g}	$A_{1g}+A_{2g}+E_{2g}$	$B_{1g}+B_{2g}+E_{1g}$
E_{2u}	E_{2u}	E_{2u}	E_{1u}	E_{1u}	$B_{1u}+B_{2u}+E_{1u}$	$A_{1u}+A_{2u}+E_{2u}$	E_{2g}	E_{2g}	E_{1g}	E_{1g}	$B_{1g}+B_{2g}+E_{1g}$	$A_{1g}+A_{2g}+E_{2g}$

Vibronically allowed transitions

We know that
$$\Gamma_{homo} \otimes \Gamma_{lumo} = b_{1u} \text{ or } b_{2u}$$
and
$$\Gamma_{x,y \text{ or } z} = e_{1u} \text{ or } a_{2u}$$
If we consider a z-polarized (out-of-plane) transition we have:
$$b_{1u} \otimes \Gamma_{vib} = a_{2u} \quad \text{or} \quad b_{2u} \otimes \Gamma_{vib} = a_{2u}$$
Using the product table we see that the modes that satisfy these equations are b_{2g} and b_{1g}, respectively.

If we consider an x,y-polarized (in-plane) transition we have:
$$b_{1u} \otimes \Gamma_{vib} = e_{1u} \quad \text{or} \quad b_{2u} \otimes \Gamma_{vib} = e_{1u}$$
Using the product table we see that the only mode that satisfies these equations has e_{2g} symmetry. This is the most likely vibronic mode.

Vibrational analysis of benzene

Using DFT methods we calculated the vibrational frequencies of benzene. The normal mode displacements were calculated and then plotted. Three important cases are shown on the following slide. Displacements in the excited state potential energy surface were observed for the A_{1g} modes only. No displacements were observed for non-totally symmetric modes such as e1u. However, vibronic modes such as e_{2g} (predicted using group theory!) show a typical double well potential.

The absorption spectrum and resonance Raman spectrum were calculated using the program TIMETHERM based on the excited state displacements.
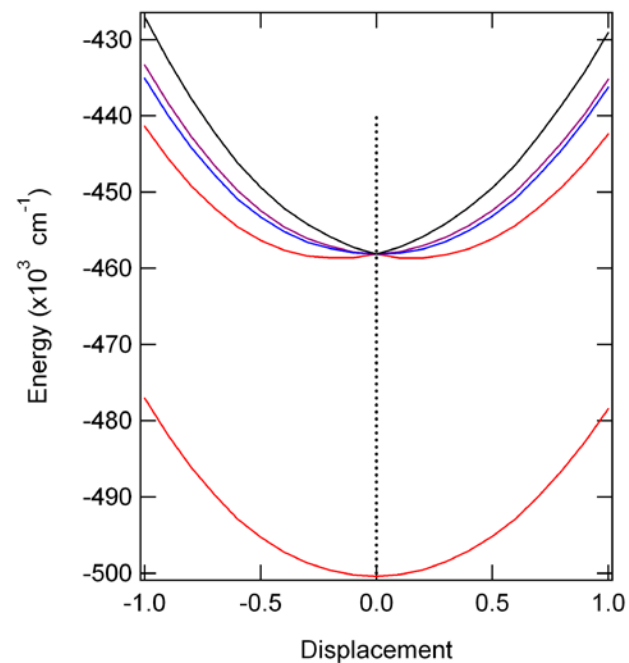
Potential energy surfaces
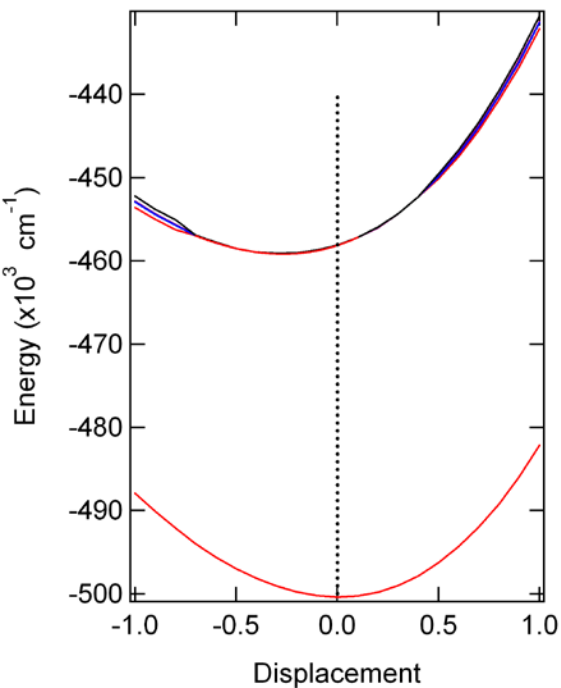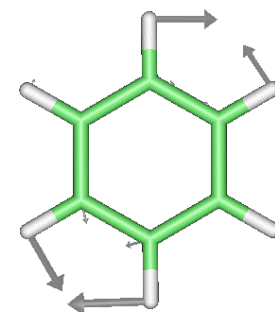

Shifted
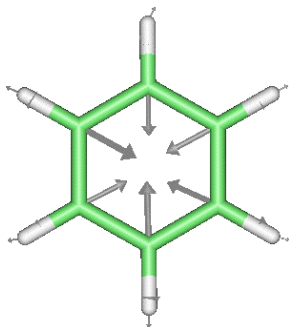
A_{1g} 1101 cm^{-1}
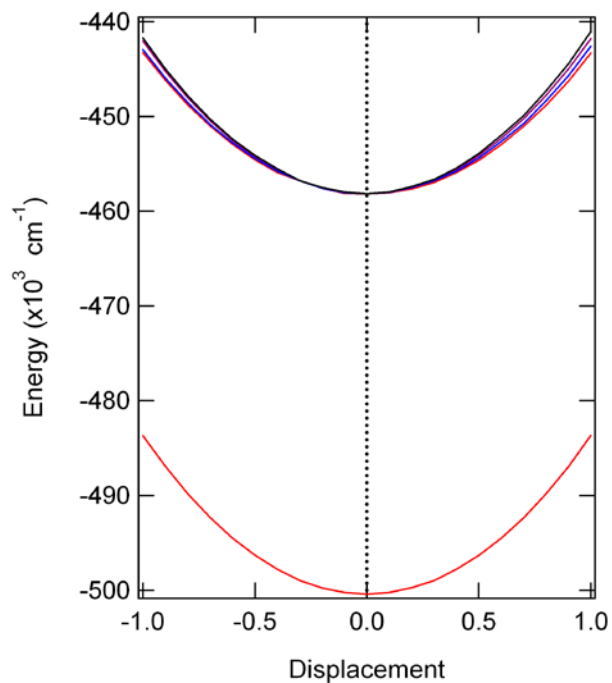
Unshifted
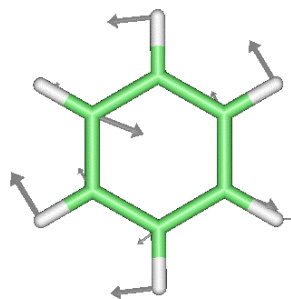
E_{1u} 1035 cm^{-1}

Vibronic

E_{2g} 1141 cm^{-1}

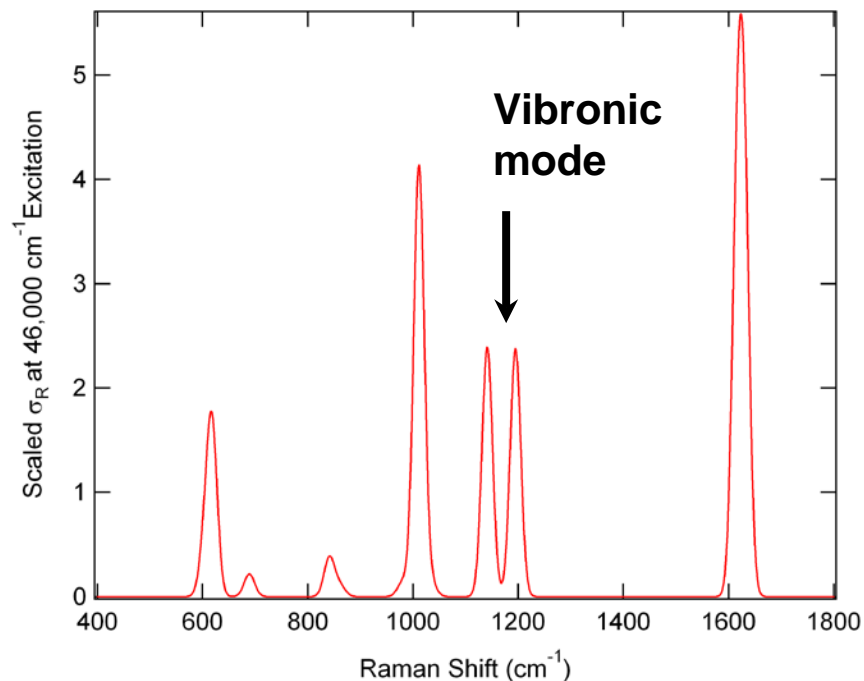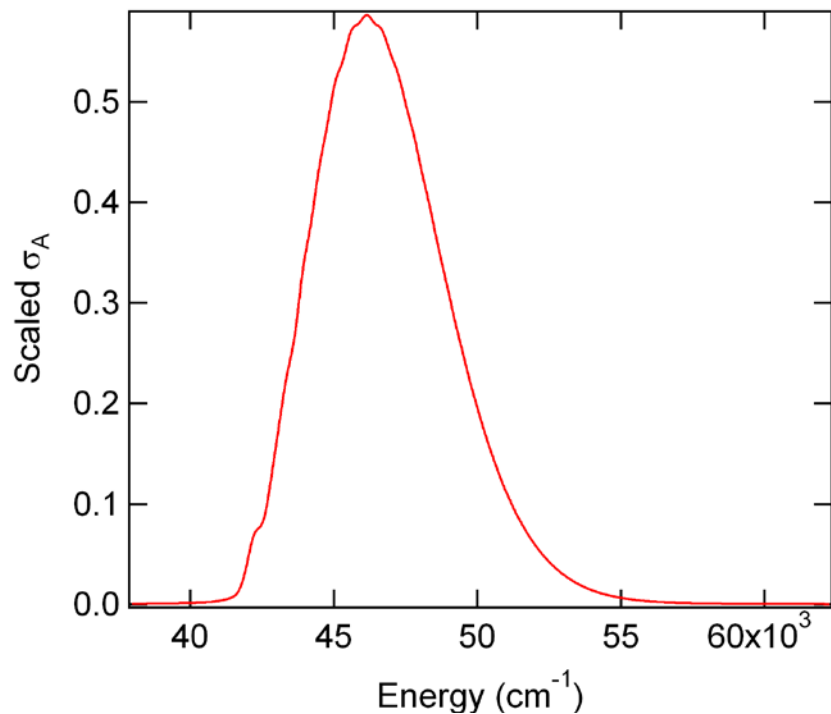# Calculated Benzene Absorption and Raman Spectra

Line broadening is added artificially based on experimental spectral widths.