

Quantum Chemistry

Lecture 7 Group Theory

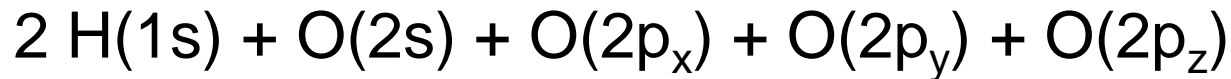
Application to the LCAO
Approach to MO Theory

NC State University

Polyatomic molecules: H₂O

For polyatomic molecules appropriate atomic orbitals must be combined into symmetry adapted linear combinations (SALCs). We can identify two groups of atoms in H₂O. The central O atom (group 1) and the pair of H atoms (group 2).

H₂O belongs to the C_{2v} point group. We have already seen that group 1 consists of the valence orbitals of the O atom:



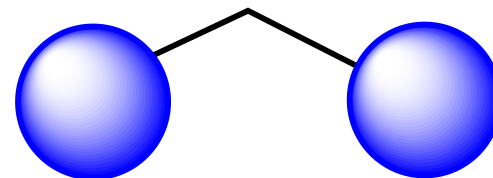
Since the oxygen is unmoved by every symmetry operation the character can be determined directly from the character table. However, the hydrogens need to be formed as SALCs first.

Reducible rep for the H atoms

To treat the H atoms we look at the set of two H atoms, each having 1s orbital. First we can consider the Reducible representation for the two 1s orbitals.

C_{2v} character table and the reducible representation for the 2H(1s) orbitals in water

C_{2v}	E	C_2	$*_v(xz)$	$*_v(yz)$	
A_1	1	1	1	1	z
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	x
B_2	1	-1	-1	1	y
$*[H(1s)]$	2	0	2	0	



When we decompose this reducible representation we find:

$$\chi_{A_1} = \frac{1}{4} ((1)(2)(1) + (1)(0)(1) + (1)(2)(1) + (1)(0)(1)) = 1$$

$$\chi_{A_2} = \frac{1}{4} ((1)(2)(1) + (1)(0)(1) + (-1)(2)(1) + (1)(0)(1)) = 0$$

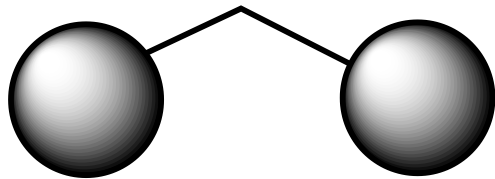
$$\chi_{B_1} = \frac{1}{4} ((1)(2)(1) + (-1)(0)(1) + (1)(2)(1) + (-1)(0)(1)) = 1$$

$$\chi_{B_2} = \frac{1}{4} ((1)(2)(1) + (-1)(0)(1) + (-1)(2)(1) + (1)(0)(1)) = 0$$

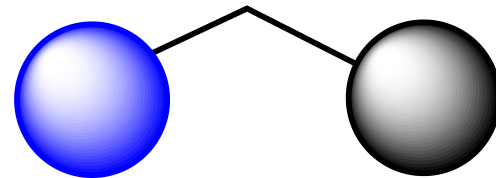
Linear combinations of H atoms

We can use a method known as projection operators to
Determine what the linear combinations of H atoms
Correspond to in terms of symmetry adapted atomic orbitals.

These are easily visualized in this case:



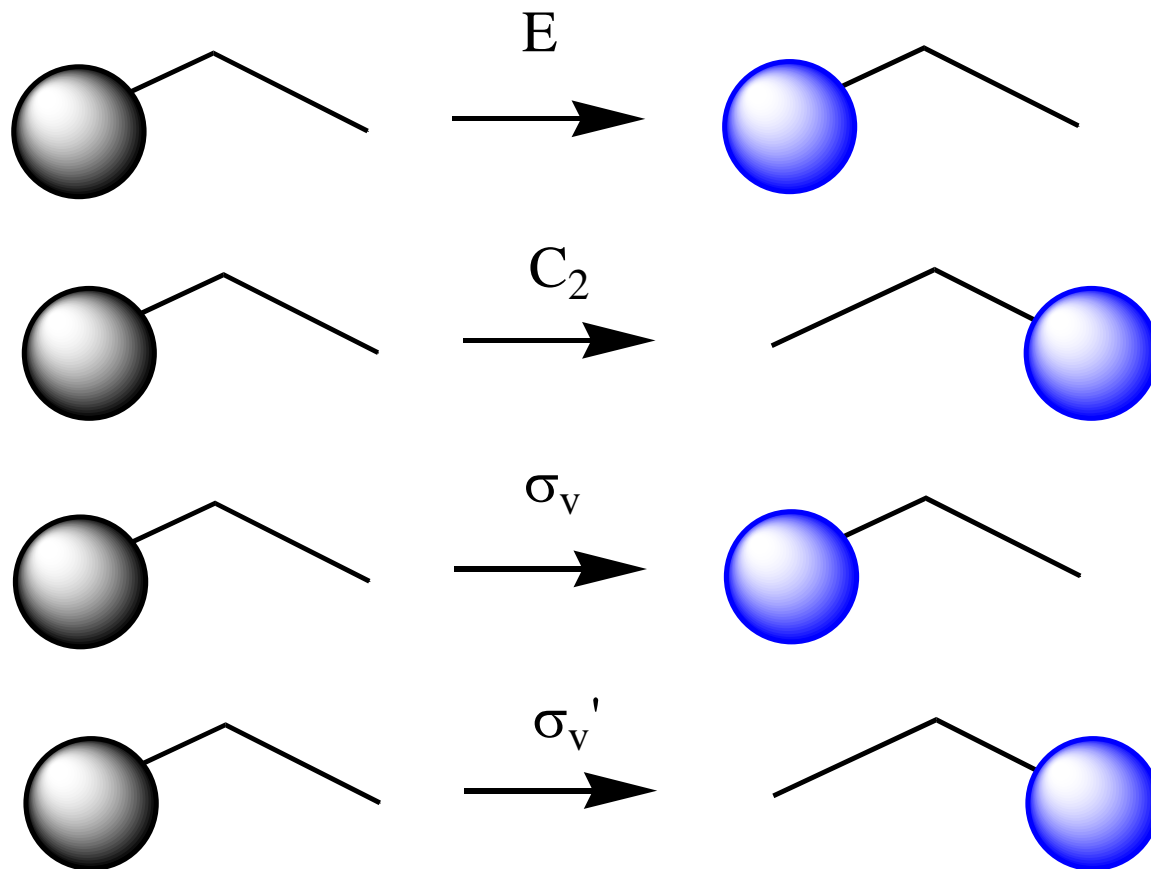
$$\chi_{A_1} = 1s_A + 1s_B$$



$$\chi_{B_1} = 1s_A - 1s_B$$

Method of Projection Operators

To use the projection operator method we choose one member of a symmetry related set of orbitals. We then apply the symmetry operations of the group to that orbital and observe how that AO is transformed into other orbitals in the molecule.



Method of Projection Operators

We can see that H_2 either remains in its location or is transformed into H_3 by the symmetry operations. Thus, we find that a table would look like

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$
P	H_2	H_3	H_2	H_3
A_1	1	1	1	1
B_1	1	-1	1	-1

The row labeled P shows the projections. Finally, we apply the characters of the irreps for that set to construct MOs. We determined that there are two MOs, which transform as a_1 and b_1 . We multiply the projected AOs by the characters of these irreps to find the two linear combinations.

Polyatomic molecules

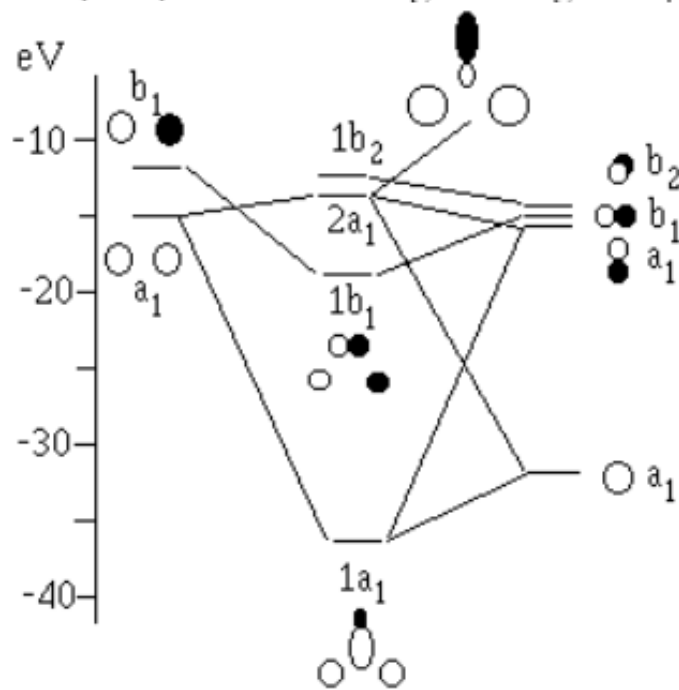
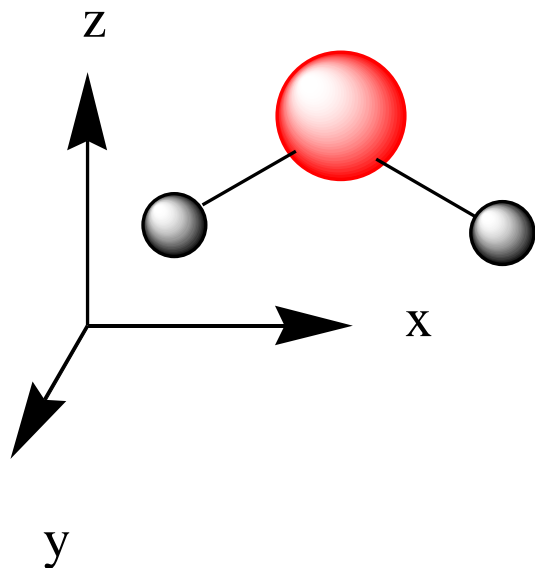
The reducible representations for hydrogen SALCs are a_1 and b_1 . The oxygen orbitals (read from the character Table) are:

$$2s = a_1$$

$$2p_z = a_1$$

$$2p_x = b_1$$

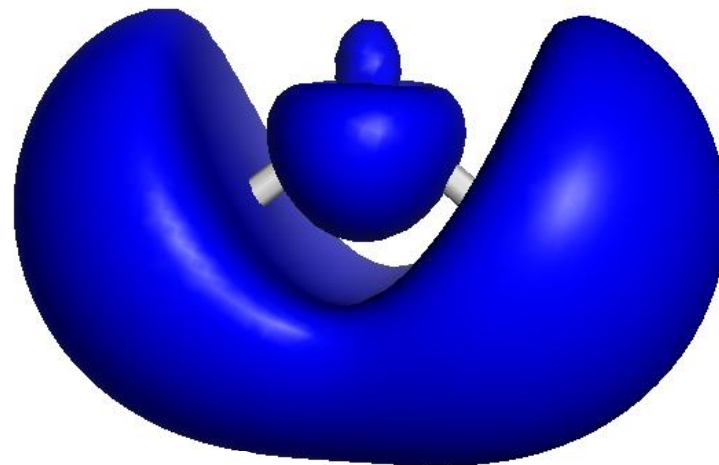
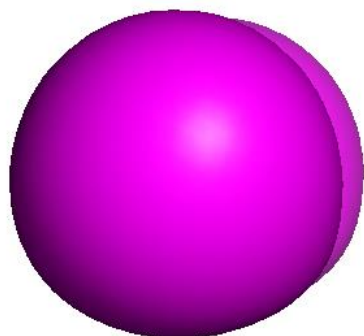
$$2p_y = b_2$$



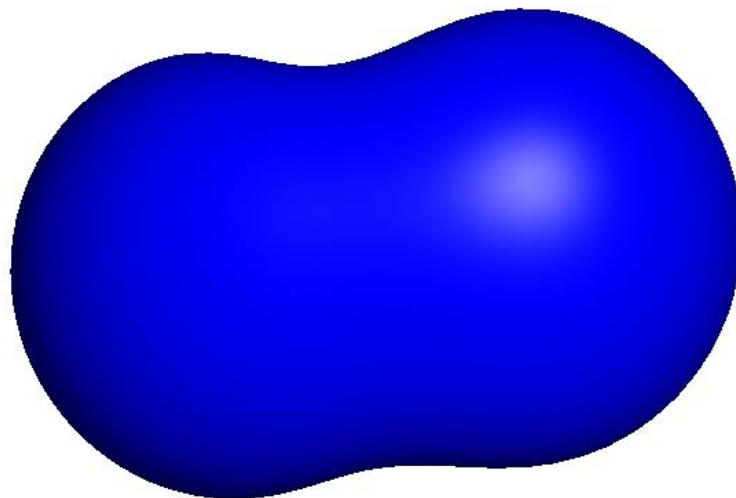
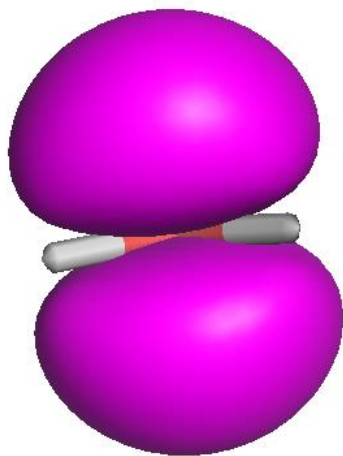
Note that the energies are obtained from a calculation. However, the forms of the orbitals can be predicted based on symmetry considerations.

HOMO to LUMO transition in H₂O

top



side



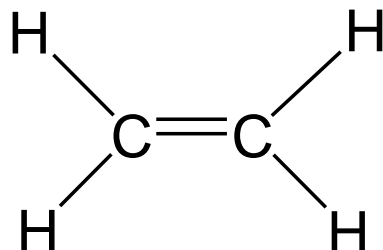
b₂

a₁

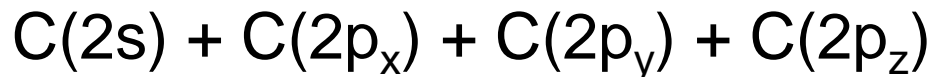
Eigenstate		Irrep	Hartrees	eV	Occupation	
1	+	1	a1.1	-18.748477	-510.1	1.000
2	-	1	a1.1	-18.748477	-510.1	1.000
3	+	2	a1.1	-0.917545	-24.968	1.000
4	-	2	a1.1	-0.917545	-24.968	1.000
5	+	1	b1.1	-0.471788	-12.838	1.000
6	-	1	b1.1	-0.471788	-12.838	1.000
7	+	3	a1.1	-0.333240	-9.068	1.000
8	-	3	a1.1	-0.333240	-9.068	1.000
9	+	1	b2.1	-0.253144	-6.888	1.000
10	-	1	b2.1	-0.253144	-6.888	1.000
11	+	4	a1.1	0.023886	0.650	0.000
12	-	4	a1.1	0.023886	0.650	0.000
13	+	2	b1.1	0.093912	2.555	0.000
14	-	2	b1.1	0.093912	2.555	0.000
19	+	2	b2.1	0.563271	15.327	0.000
20	-	2	b2.1	0.563271	15.327	0.000
27	-	1	a2.1	0.926496	25.211	0.000
28	+	1	a2.1	0.926496	25.211	0.000

Ethene

Molecules with p-systems are particularly important in Organic chemistry. The simplest of these is ethene.

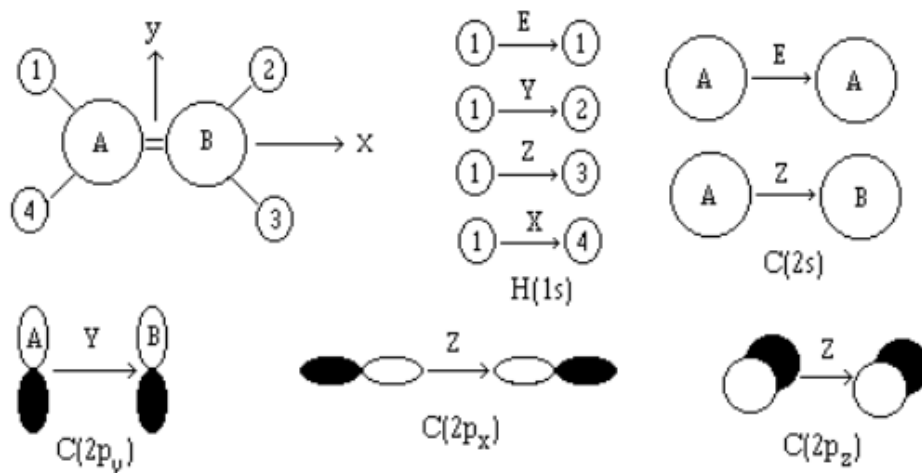


Ethene belongs to the D_{2h} point group. The carbons are symmetrically equivalent. The orbital set on each consists of



Ethylene

The atomic orbitals are shown below:



The reducible representations of the symmetrically equivalent sets formed for the valence ao's of ethylene can be determined and decomposed in the following groups.

D _{2h}	E	Z	Y	X	i	XY	XZ	YZ	Irreps
H(1s)	4	0	0	0	0	4	0	0	a _g +b _{1g} +b _{2u} +b _{3u}
C(2s)	2	0	0	2	0	2	2	0	a _g + b _{3u}
C(2p _z)	2	0	0	-2	0	-2	2	0	b _{2g} + b _{1u}
C(2p _x)	2	0	0	2	0	2	2	0	a _g + b _{3u}
C(2p _y)	2	0	0	-2	0	2	-2	0	b _{1g} + b _{2u}

Ethylene

Since the members of all of the sets can be exchanged completely with only the rotational operations, only the C_2 characters of the above character table need be considered

D_{2h}	E	Y	Z	X
a_g	+1	+1	+1	+1
b_{1g}	+1	-1	+1	-1
b_{2g}	+1	+1	-1	-1
b_{1u}	+1	-1	+1	-1
b_{2u}	+1	+1	-1	-1
b_{3u}	+1	-1	-1	+1

The set E, X, Y, Z correspond to the H atoms in ethene. We can use the table above to construct the SALCs for the irreps that were determined.

Ethene

The normalized SALCs can now be constructed:

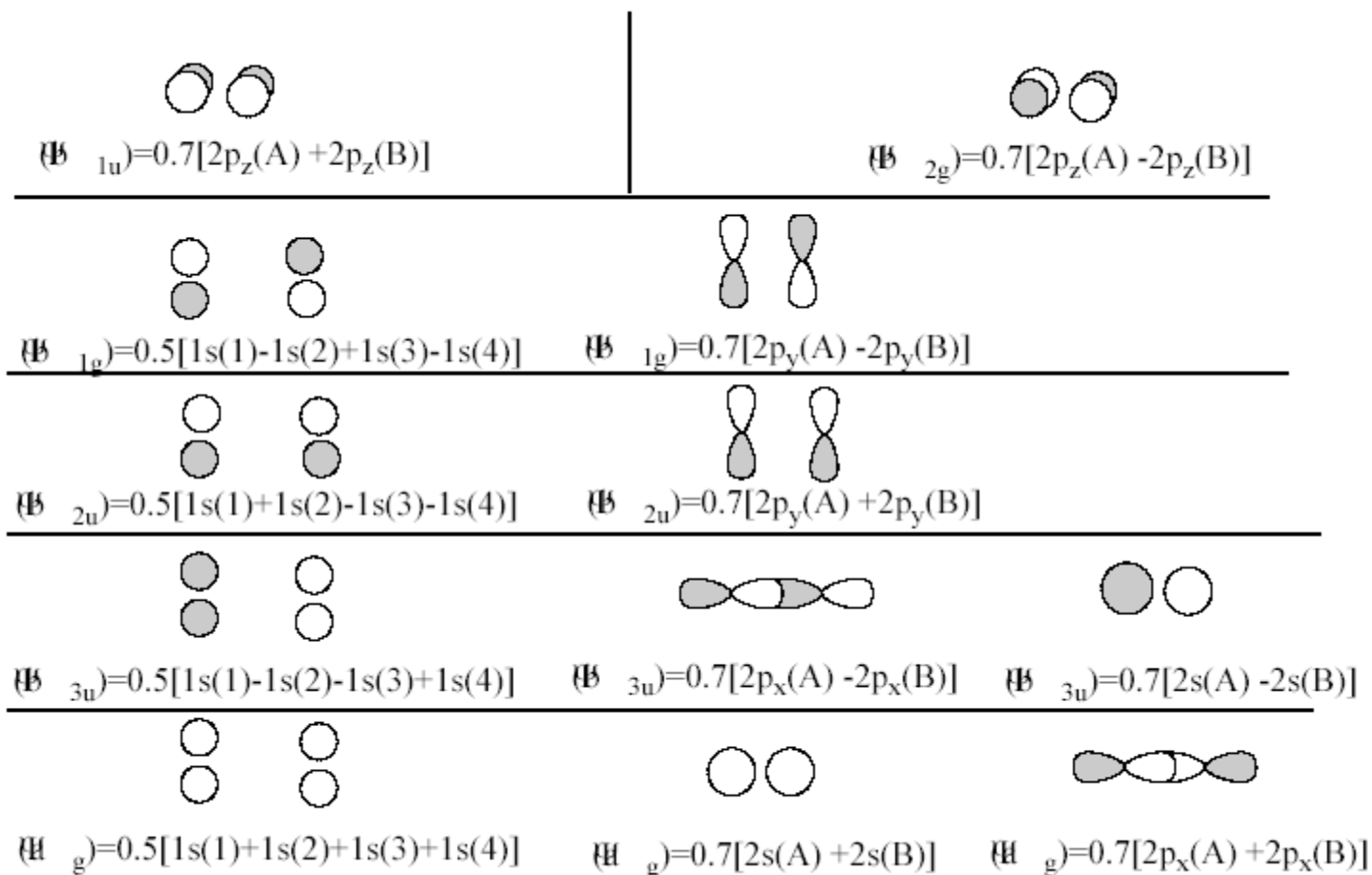
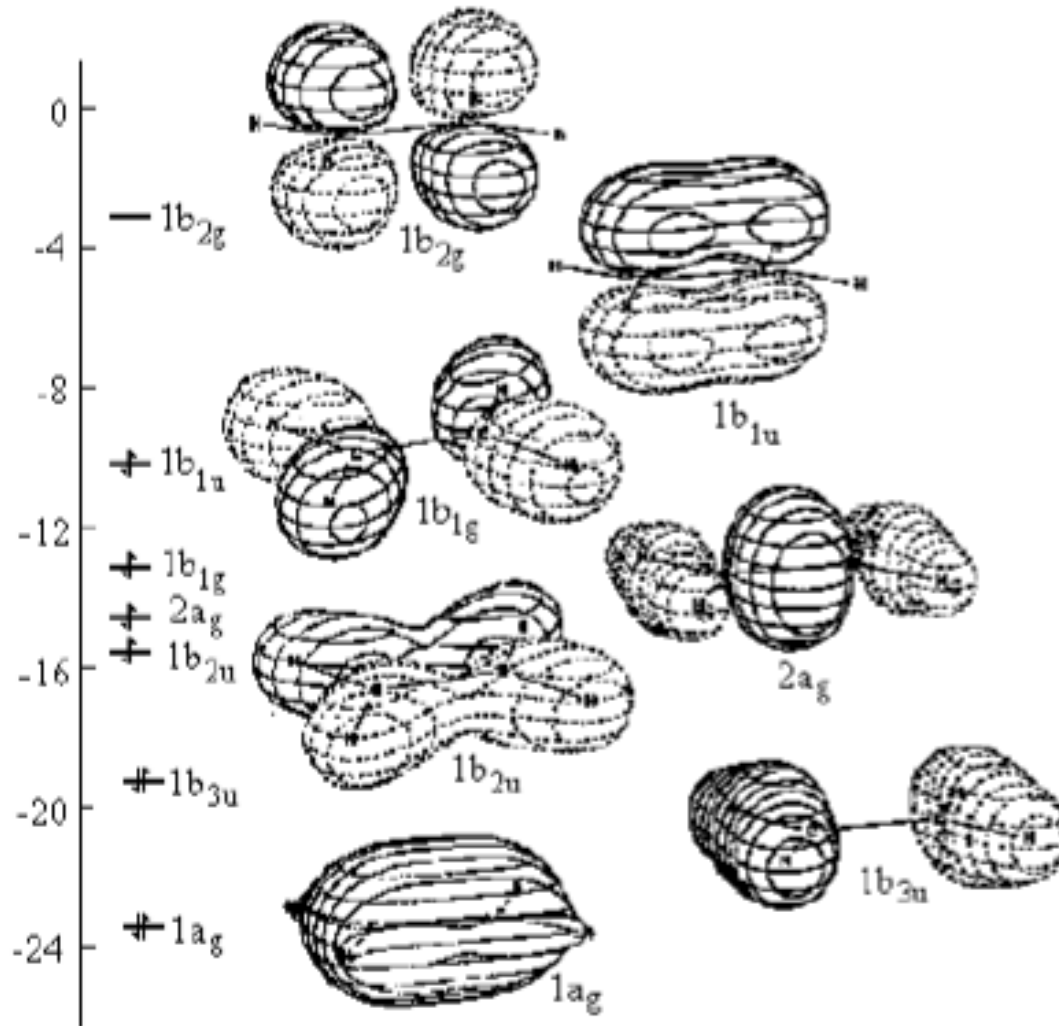


Figure II.13. The normalized SALC's for the ethylene molecule.

Ethene

The normalized SALCs can now be constructed:



1	a_g	-268.881	2
2	b_{1u}	-268.863	2
3	a_g	-18.668	2
4	b_{1u}	-14.148	2
5	b_{2u}	-11.376	2
6	a_g	-10.115	2
7	b_{3g}	-8.464	2
8	b_{3u}	-6.613	2
9	b_{2g}	-0.817	0
10	a_g	2.541	0
11	b_{2u}	2.612	0
12	b_{1u}	3.337	0
13	b_{3g}	5.499	0
14	b_{2g}	13.552	0

Transition moment for ethene

Note that the issue with this calculation is that the coordinate system in the quantum chemistry program is not the same as the one in the textbook example.

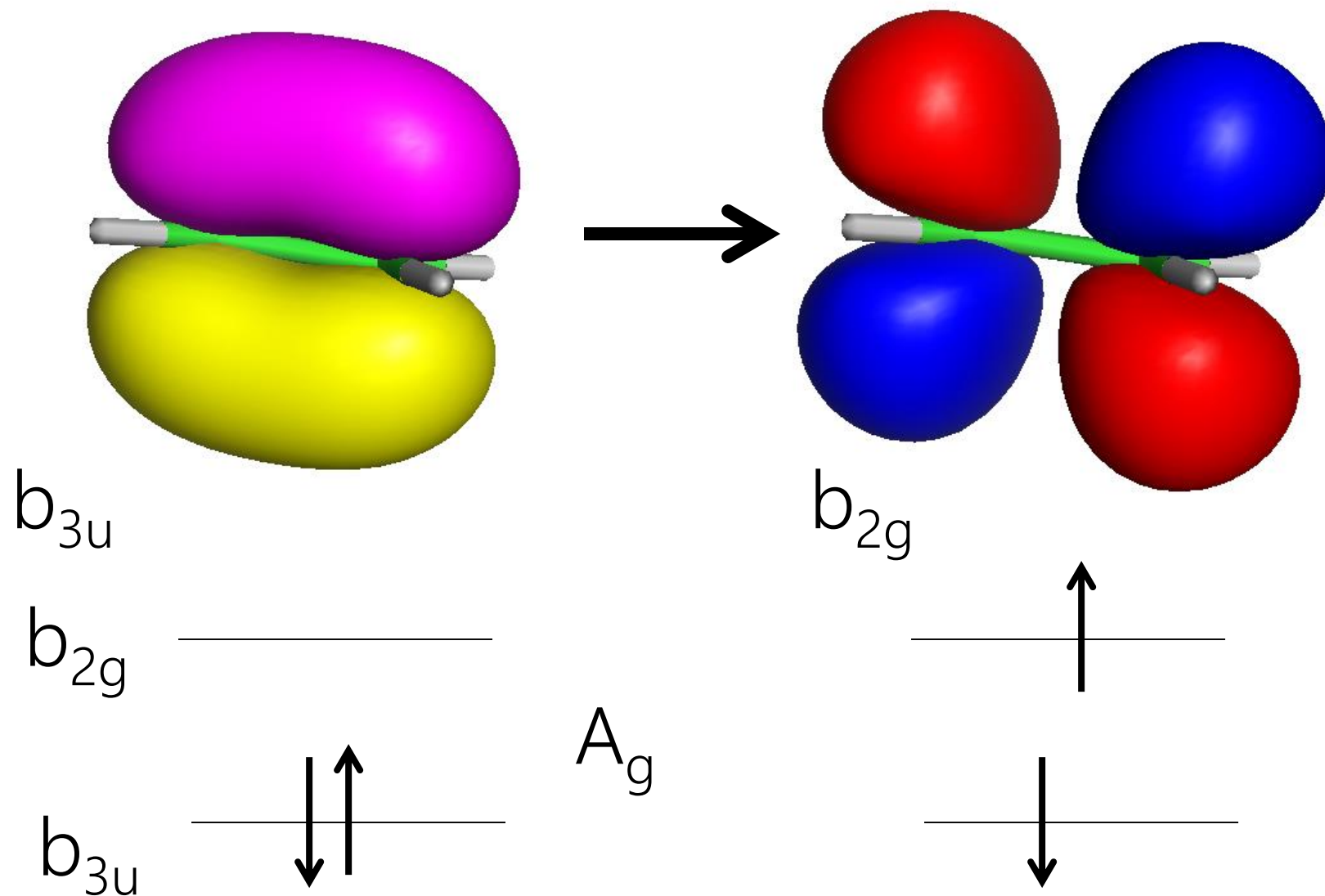
Question: which polarization of electromagnetic radiation can excite the $b_{3g} \rightarrow b_{2u}$ transition?

Answer: An allowed transition must have transition moment that contains the totally symmetric representation. In the D_{2h} point group this means that the direct product

$$\Gamma_g \Gamma_{EM} \Gamma_e = A_{1g}$$

One way to find this is to calculate the direct product for each basis vector that contains x, y or z.

MO diagram for the HOMO and LUMO



Polarization of the allowed transition

Rather than try three different direct products, it is effective to note that the A_g product will be achieved if

$$\Gamma_g \Gamma_e = \Gamma_x \text{ or } \Gamma_y \text{ or } \Gamma_z$$

In this case, we can calculate the direct product from the known HOMO and LUMO irreducible representations.

The direct product of B_{3u} and B_{2g} is

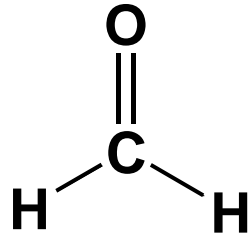
D_{2h}	E	C_2	C_2'	C_2''	i	σ_v	σ_v'	σ_v''
B_{3u}	1	-1	-1	1	-1	1	1	-1
B_{2g}	1	-1	1	-1	1	-1	1	-1
Γ_{trans}	1	1	-1	-1	-1	-1	1	1

We can see by inspection that $\Gamma_{\text{trans}} = B_{1u}$.

D_{2h}	E	C_2	C_2'	C_2''	i	σ_v	σ_v'	σ_v''
A_g	1	1	1	1	1	1	1	1
B_{1g}	1	1	-1	-1	1	1	-1	-1
B_{2g}	1	-1	1	-1	1	-1	1	-1
B_{3g}	1	-1	-1	1	1	-1	-1	1
A_u	1	1	1	1	-1	-1	-1	-1
B_{1u}	1	1	-1	-1	-1	-1	1	1
B_{2u}	1	-1	1	-1	-1	1	-1	1
B_{3u}	1	-1	-1	1	-1	1	1	-1

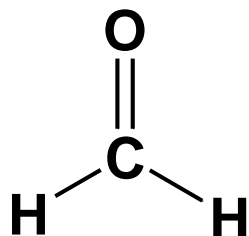
The character table tells us that that B_{1u} corresponds to a polarization along x (where x is the internuclear bond vector).

Formaldehyde



In the case of formaldehyde there is one additional atom beyond the water example in C_{2v} . Therefore, we now have three symmetry related sets. The O, C and H atoms. However, the symmetry of the C and O atoms are the same since they both lie along the symmetry axis. Thus, we can construct three different sets of symmetry adapted atomic orbitals and then combine them.

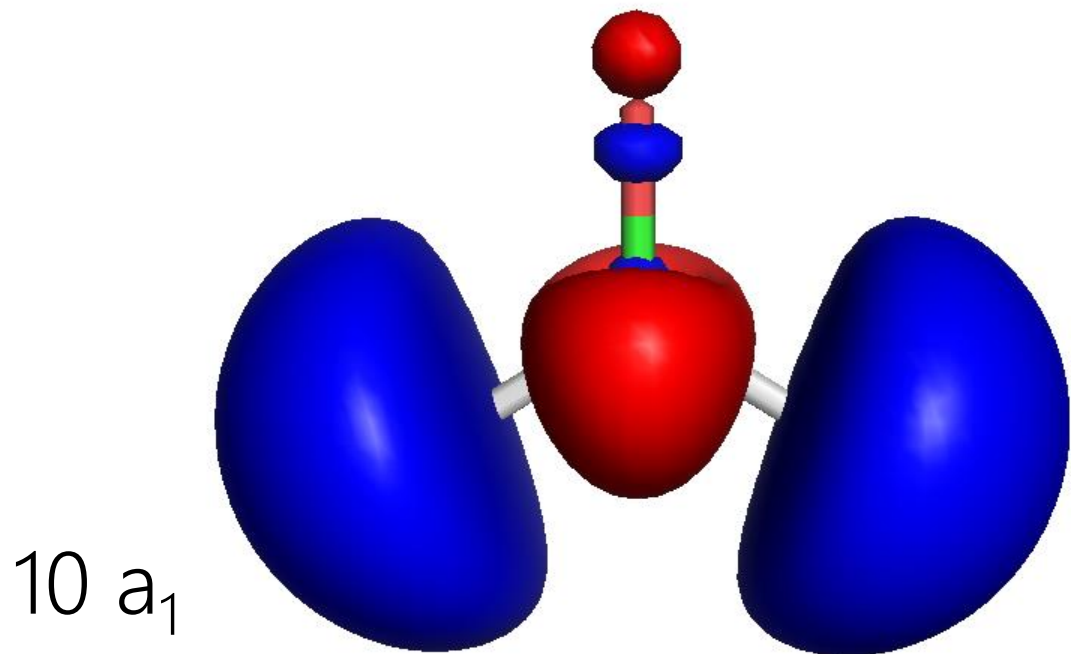
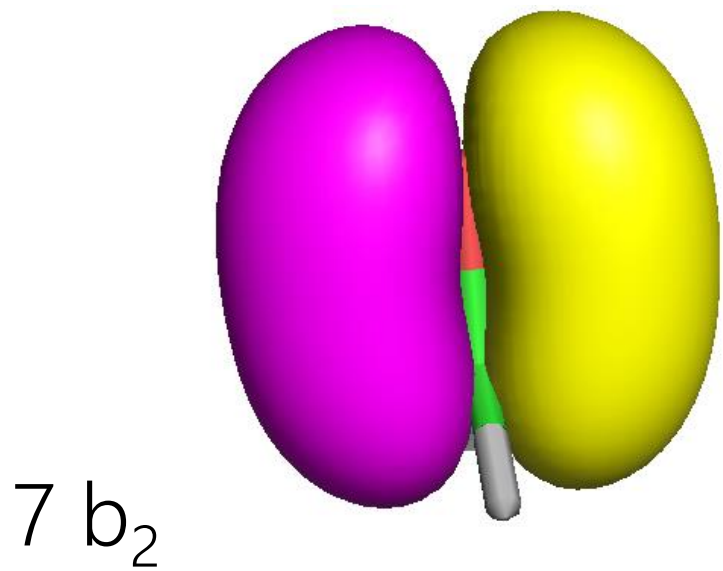
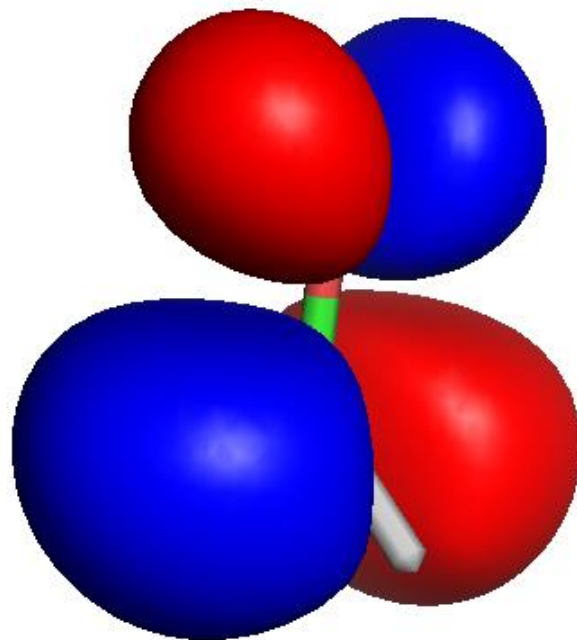
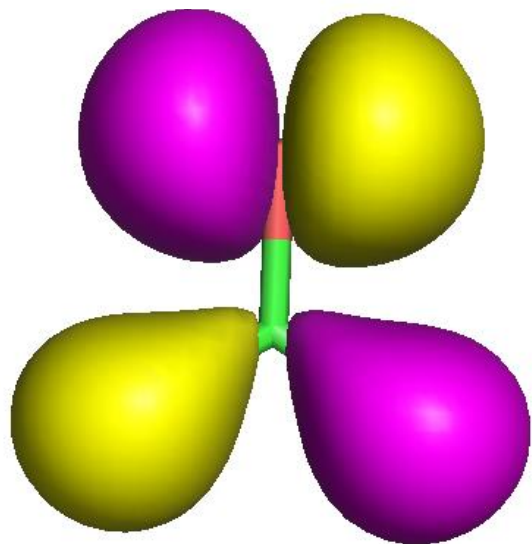
Formaldehyde



We can that the
HOMO (b_1) to LUMO (b_2)
Transition is forbidden.

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
B_1	1	-1	1	-1
B_2	1	-1	-1	1
A_2	1	1	-1	-1

MO	Irrep	eV	Occupation
1	a_1	-510.777	2.000
2	a_1	-271.620	2.000
3	a_1	-26.478	2.000
4	a_1	-15.675	2.000
5	b_1	-12.056	2.000
6	a_1	-10.884	2.000
7	b_2	-9.924	2.000
8	b_1	-6.190	2.000
9	b_2	-2.569	0.000
10	a_1	1.918	0.000
11	b_1	3.613	0.000
13	b_2	9.266	0.000



However, the HOMO (b_1) to NLUMO (a_1) is allowed. In that case the excitation radiation must be polarized along x (b_1), since

$$b_1 b_1 a_1 = a_1$$

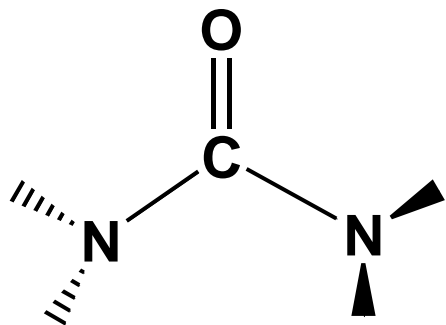
Other allowed transitions include 7 \rightarrow 9 and 8 \rightarrow 11. The direct products are,

$$b_1 b_1 = a_1 \quad \text{are} \quad b_2 b_2 = a_1$$

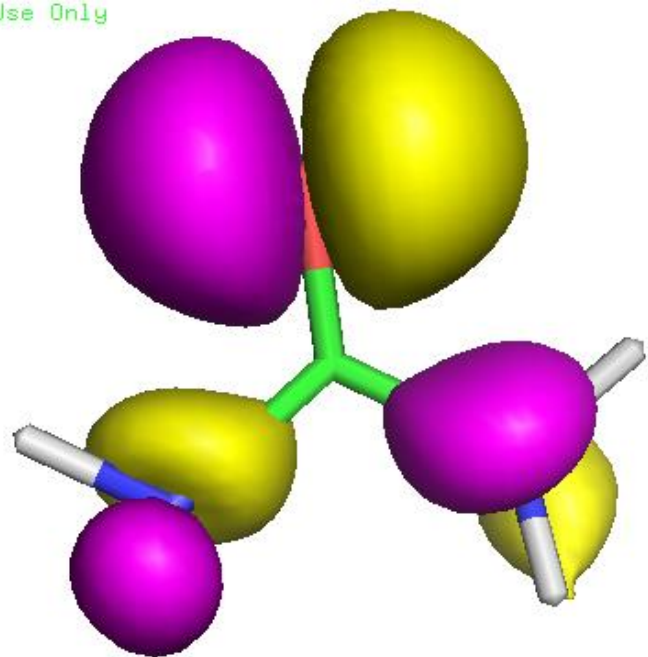
Note that a_1 corresponds to z-polarization in C_{2v} . Thus, these products tells us that the $\pi-\pi^*$ transition and n-p transition are allowed.

C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$	Rot	IR	Raman
A_1	1	1	1	1		z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z		
B_1	1	-1	1	-1	R_y	x	
B_2	1	-1	-1	1	R_x	y	

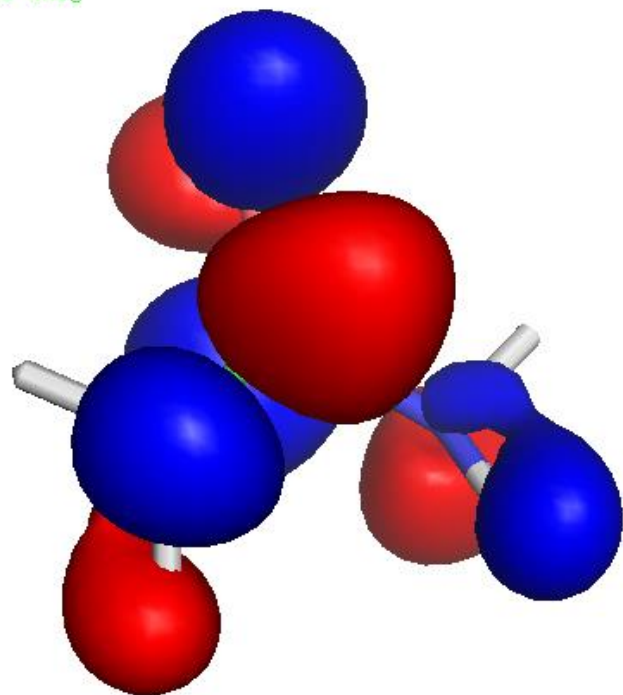
Urea



1	a	-509.064	2.000
2	b	-380.888	2.000
3	a	-380.888	2.000
4	a	-272.038	2.000
5	a	-25.833	2.000
6	a	-22.814	2.000
7	b	-21.872	2.000
8	a	-15.056	2.000
9	b	-13.468	2.000
10	a	-13.139	2.000
11	b	-11.366	2.000
12	b	-10.178	2.000
13	a	-9.805	2.000
14	a	-6.604	2.000
15	b	-6.530	2.000
16	b	-5.789	2.000
17	b	0.135	0.000
18	a	0.652	0.000

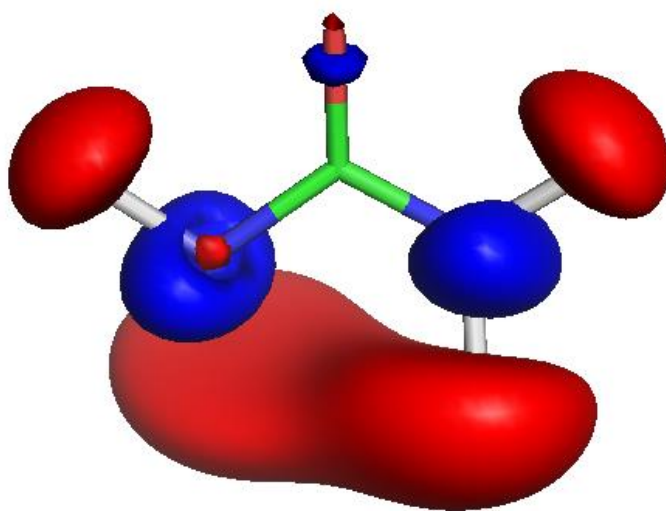


16 b



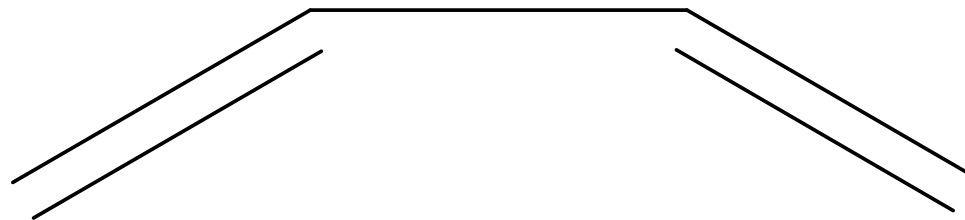
17 b

18 a



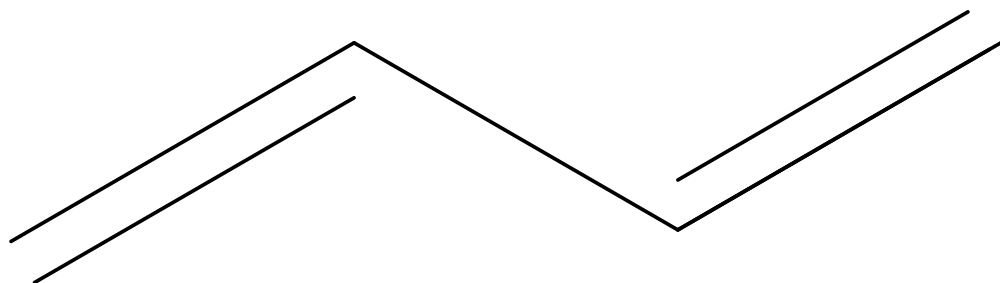
Cis and trans butadiene

cis



C_{2v}

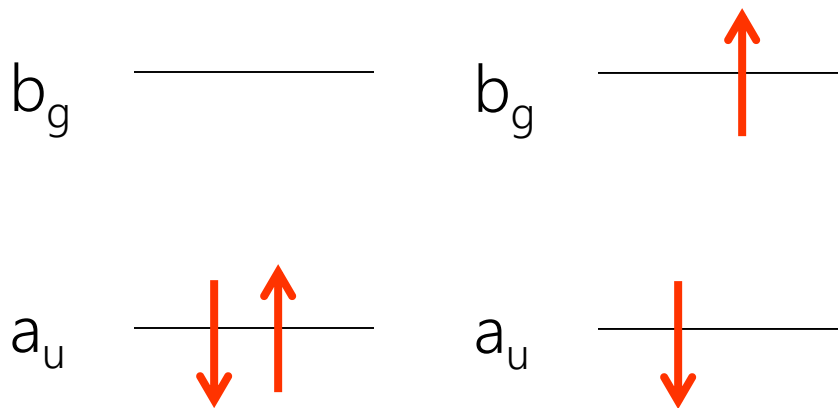
trans



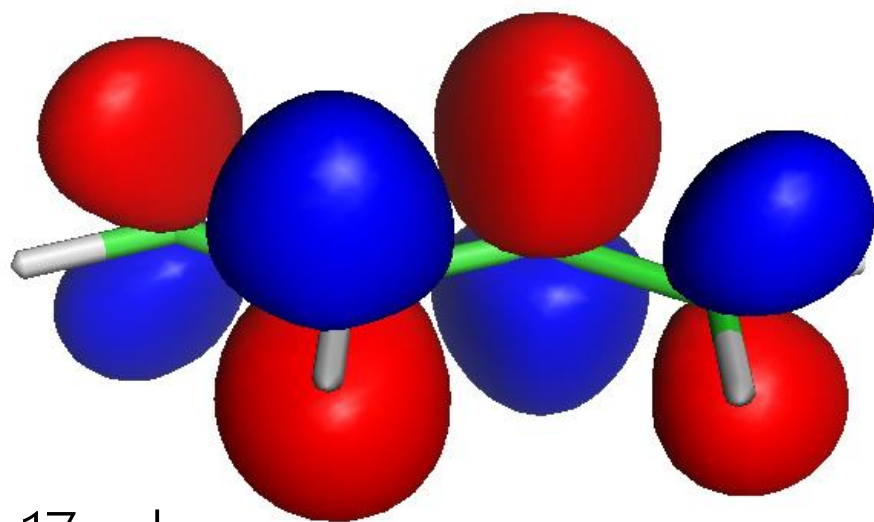
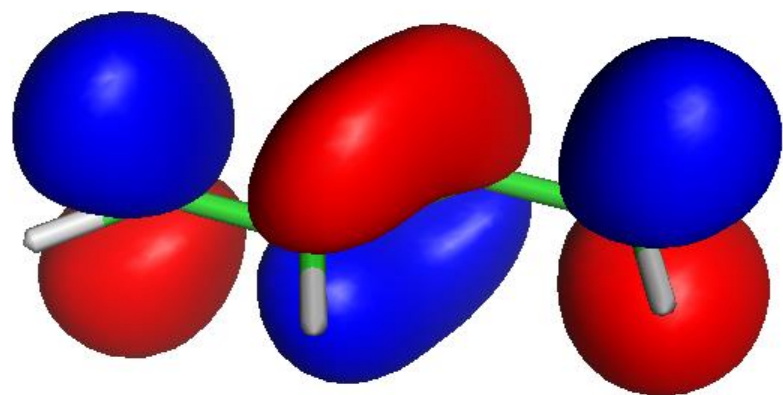
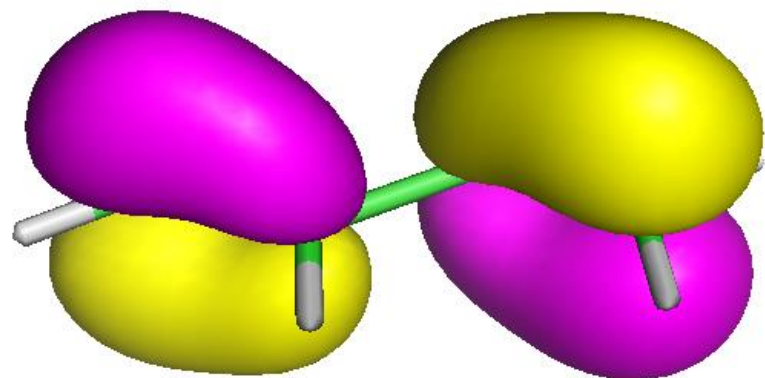
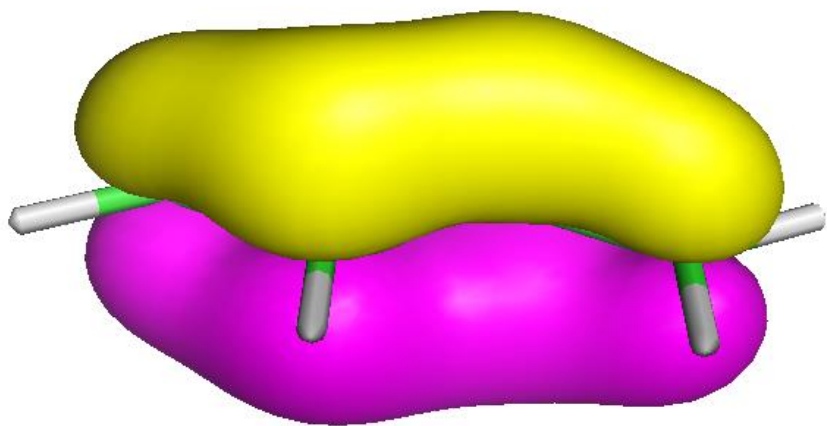
C_{2h}

Trans butadiene Molecular orbitals

C_{2h}	E	C_2	i	σ_h	linear	quadratic
A_g	1	1	1	1	R_z	$x^2, y^2, z^2,$ xy
B_g	1	-1	1	-1	R_x, R_y	xz, yz
A_u	1	1	-1	-1	z	
B_u	1	-1	-1	1	x, y	



MO	Irrep	eV	Occupation
1	a_g	-269.085	2.000
2	b_u	-269.078	2.000
3	a_g	-268.876	2.000
4	b_u	-268.875	2.000
5	a_g	-19.916	2.000
6	b_u	-18.033	2.000
7	a_g	-14.871	2.000
8	b_u	-13.504	2.000
9	b_u	-11.354	2.000
10	a_g	-11.276	2.000
11	a_g	-9.463	2.000
12	b_u	-9.299	2.000
13	a_g	-8.308	2.000
14	a_u	-7.962	2.000
15	b_g	-5.719	2.000
16	a_u	-1.783	0.000
17	b_g	0.850	0.000
18	b_u	1.932	0.000



Determining the allowed transitions of trans butadiene

C_{2h}	E	C_2	i	σ_h	linear
A_u	1	1	-1	-1	z
B_g	1	-1	1	-1	R_x, R_y
B_u	1	-1	-1	1	x, y

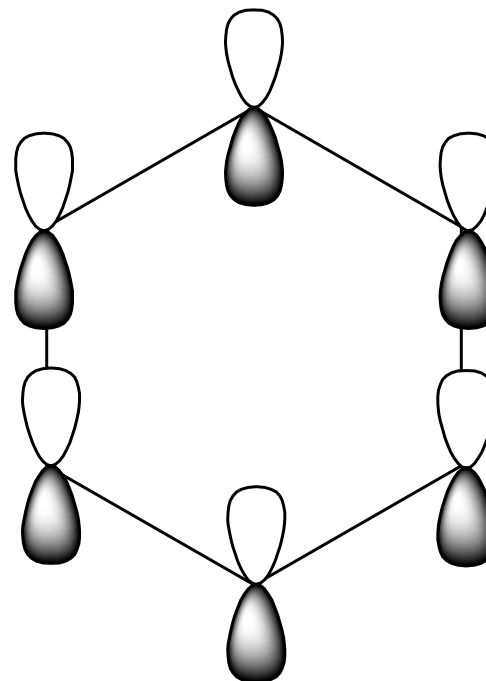
The direct product of A_u and B_g is B_u . This means that transitions are allowed along both the x and y polarizations.

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	$a_{2u}+b_{2g}+$ $e_{1g}+e_{2u}$

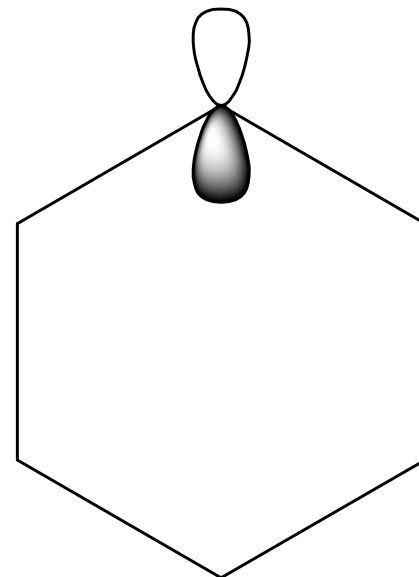
D_{6h} character table

	E	$2C_6$	$2C_3$	C_2	$3C'_2$	$3C''_2$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	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		

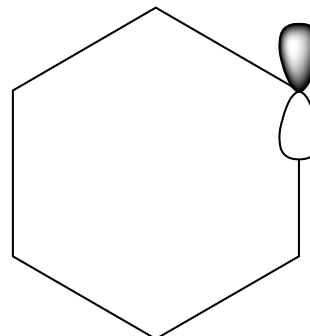
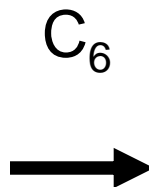
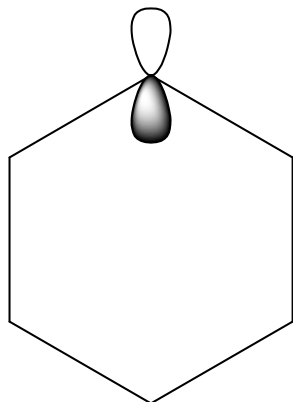
Projection operator approach

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



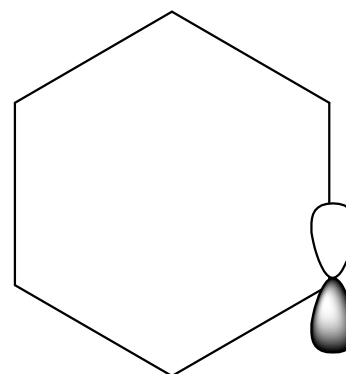
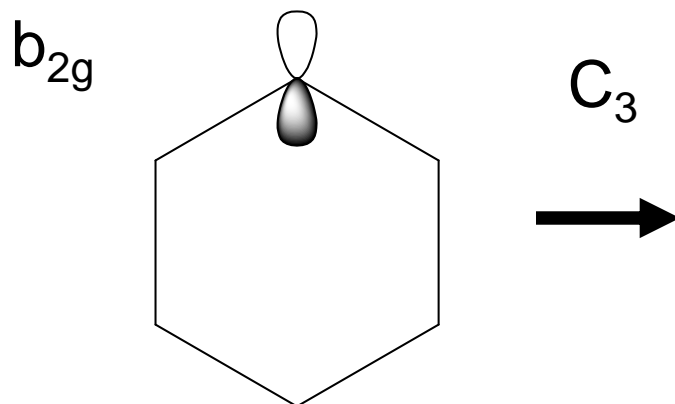
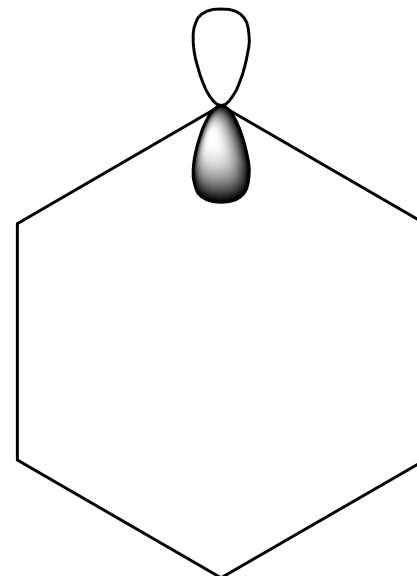
b_{2g}



Projection operator approach

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

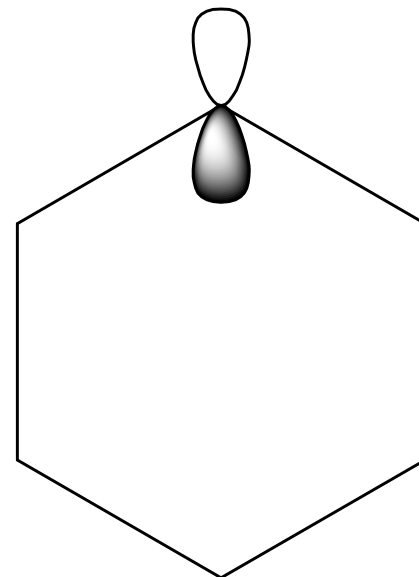
Atom	Operation	a_{2u}	b_{2g}	e_{1g}	e_{2u}
1	E	1	1	2	2
2	C_6	1	-1	1	-1
3	C_3	1	1	-1	-1
4	C_2	1	-1	-2	2
5	C_3	1	1	-1	-1
6	C_6	1	-1	1	-1



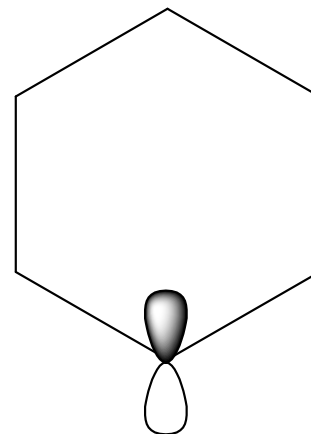
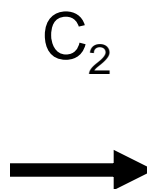
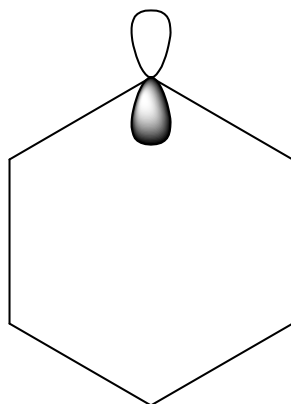
Projection operator approach

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}



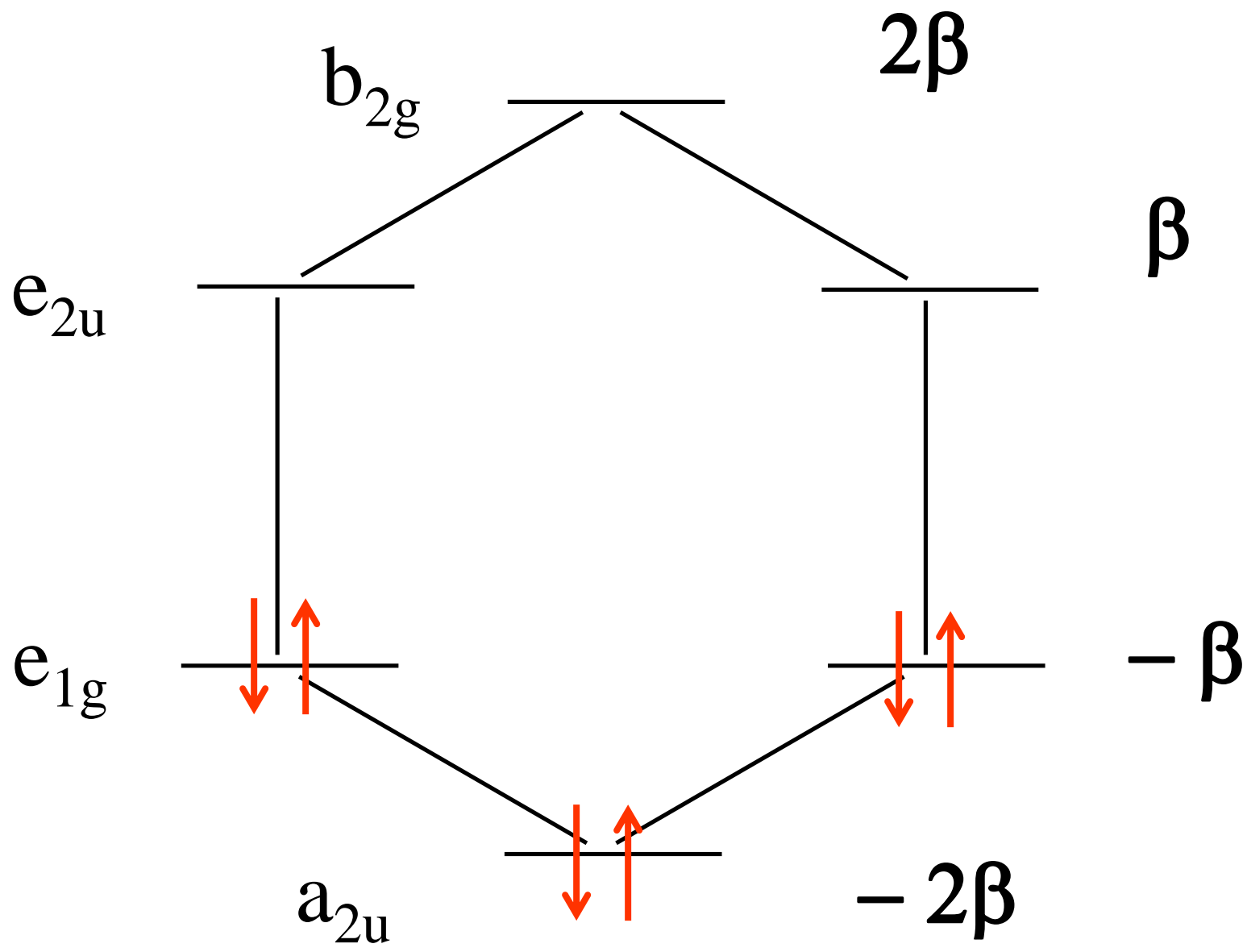
Molecular orbitals constructed using the projection operator approach

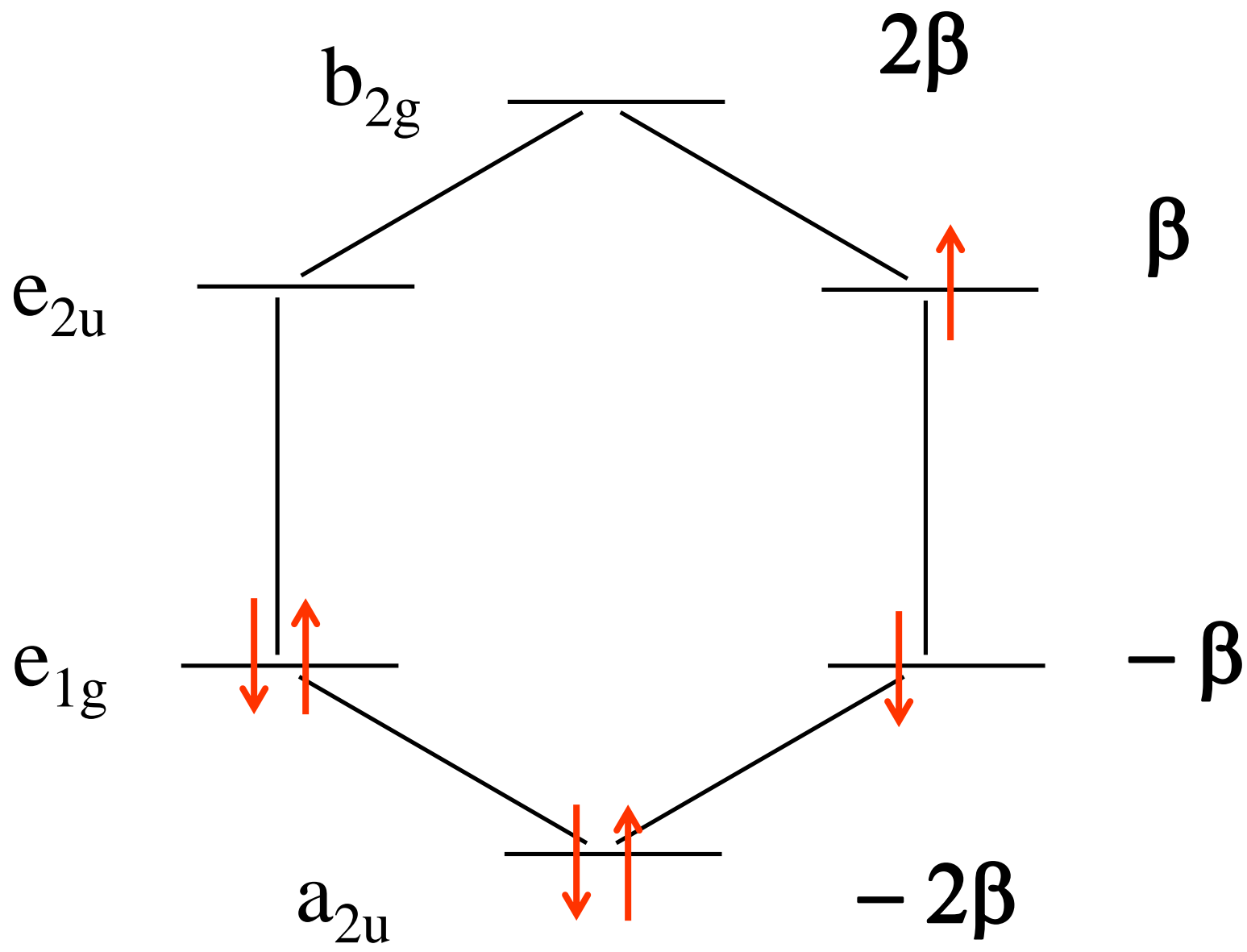
$$\Psi_{b_{2g}} = \frac{1}{\sqrt{6}}(p_1 - p_2 + p_3 - p_4 + p_5 - p_6)$$

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

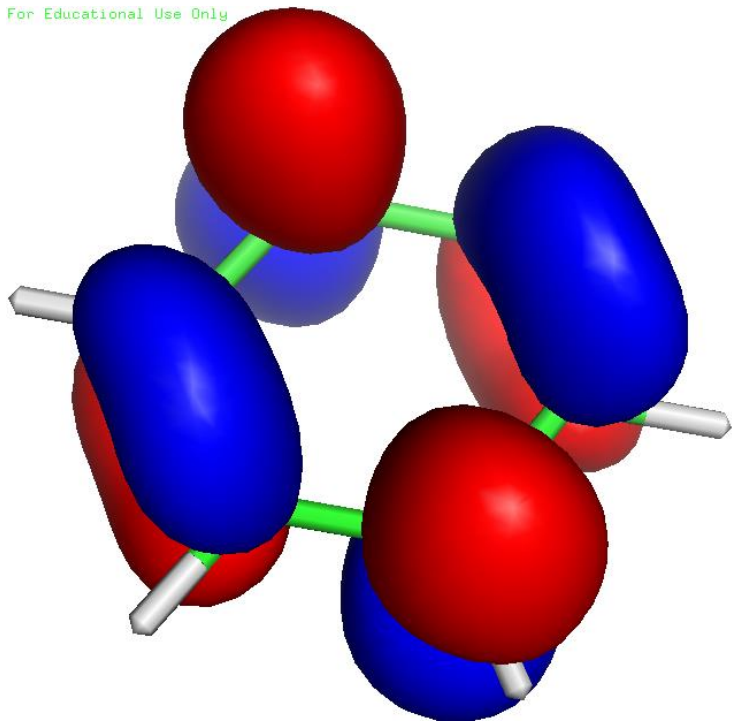
$$\Psi_{e_{1g}} = \frac{1}{\sqrt{12}}(2p_1 + p_2 - p_3 - 2p_4 - p_5 + p_6)$$

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

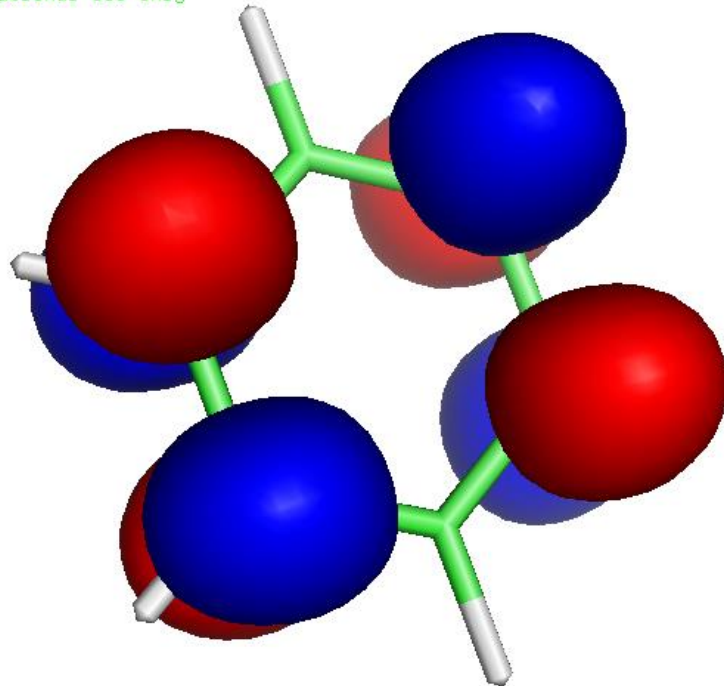




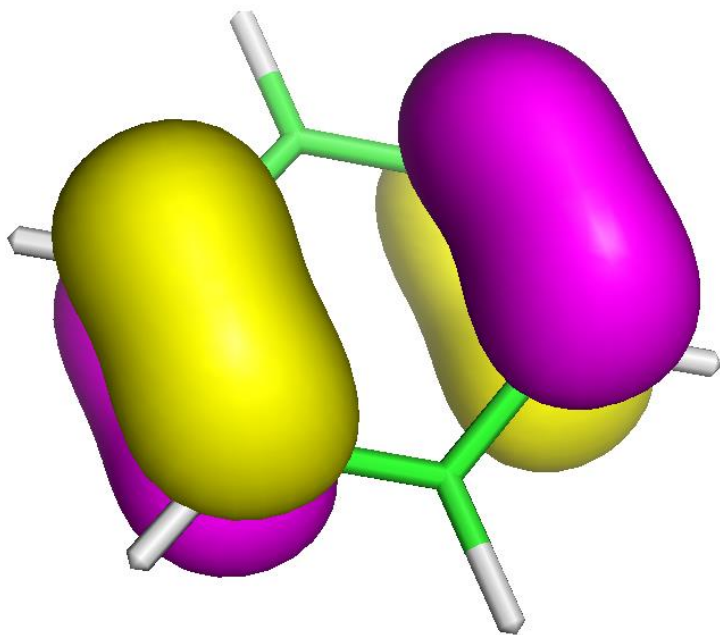
For Educational Use Only



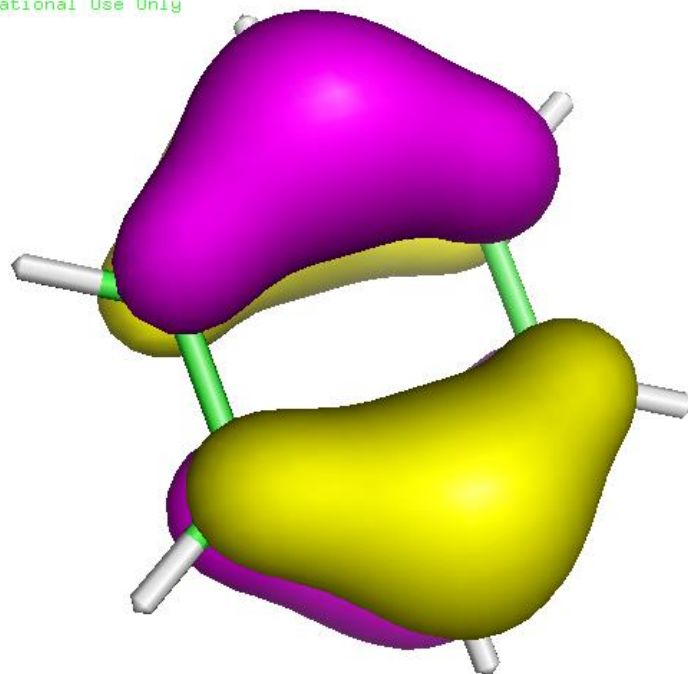
For Educational Use Only



For Educational Use Only



For Educational Use Only



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

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

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

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

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	3σ _d	3σ _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:

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

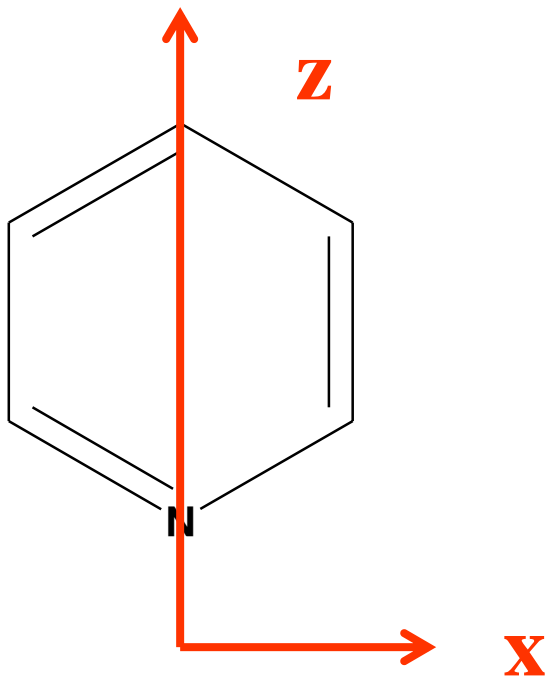
For example, in the $e_{1g} \rightarrow e_{2u}$ transition of benzene there can also be a transition that would normally be forbidden. When there are many direct products to compute it can be handy to use a product table. The next slide shows the D_{6h} product table.

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

Pyridine

Pyridine has many of the spectroscopic characteristics of Benzene. However, pyridine has the lone pair of the N atom, Which leads to the possibility of $n-\pi^*$ transitions in addition To the $\pi-\pi^*$ transitions of benzene. Pyridine belongs to the C_{2v} point group.

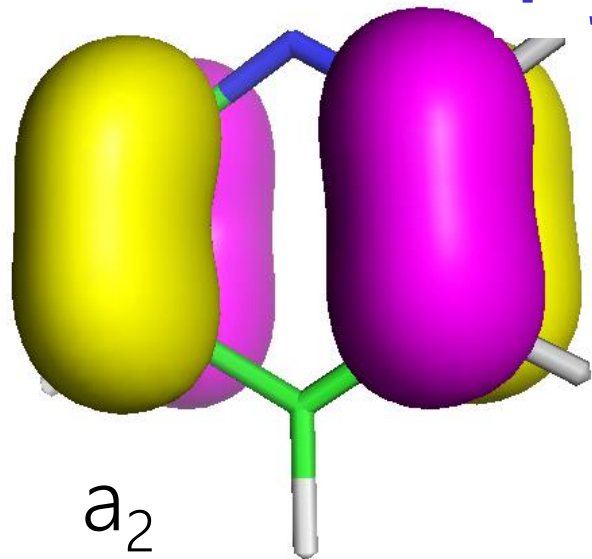


C_{2v}	E	C_2	$\sigma_{v(xz)}$	$\sigma_{v(yz)}$
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1

Pyridine

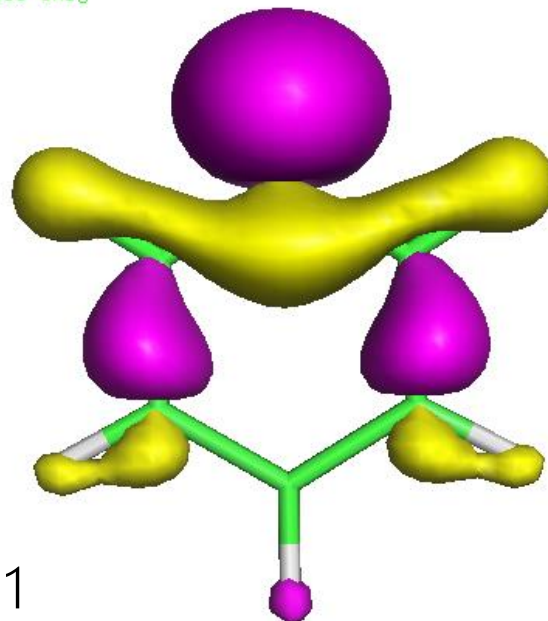
20

a_2



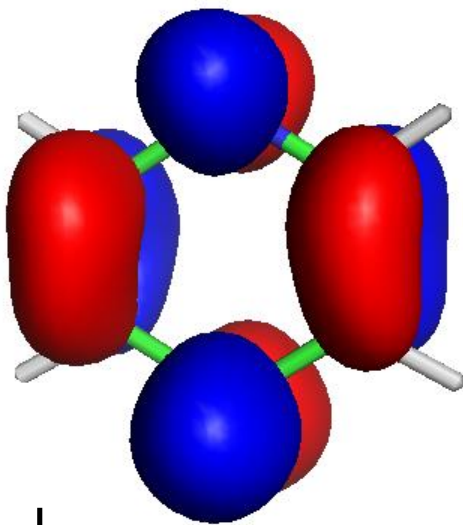
21

a_1



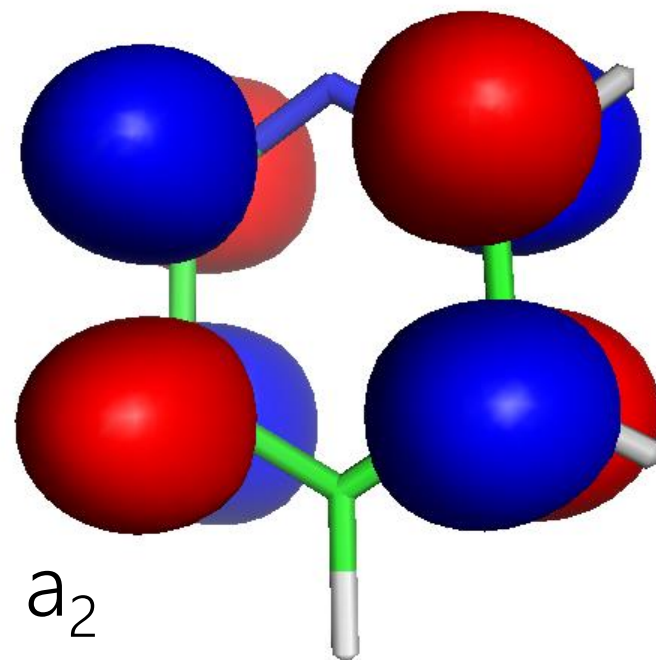
22

b_2



23

a_2



Pyridine transitions

The n- π^* is:

21 a₁ -> 22 b₂

Weak absorption 280 nm

The π - π^* transitions are similar to benzene:

19 b₂ -> 22 b₂ or 23 a₂

20 a₂ -> 22 b₂ or 23 a₂

Moderate absorption

274 nm, 230 nm

Strong absorption

169 nm

MO	Irrep	eV	Occupation
11	a ₁	-15.520	2.000
12	a ₁	-13.042	2.000
13	b ₁	-11.820	2.000
14	a ₁	-11.487	2.000
15	b ₁	-10.459	2.000
16	b ₂	-9.824	2.000
17	a ₁	-9.816	2.000
18	b ₁	-8.800	2.000
19	b ₂	-7.222	2.000
20	a ₂	-6.623	2.000
21	a ₁	-5.896	2.000
22	b ₂	-1.778	0.000
23	a ₂	-1.412	0.000
24	a ₁	1.519	0.000
25	b ₂	2.421	0.000

Product table for the C_{2v} point group

We can see that there are numerous possibilities for transitions. Using the method that

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

for an allowed transition, and recalling that x, y and z transform as b_1 , b_2 and a_1 , respectively, we can quickly determine the allowed transitions and polarizations using a C_{2v} product table.

	A_1	A_2	B_1	B_2
A_1	A_1	A_2	B_1	B_2
A_2	A_2	A_1	B_2	B_1
B_1	B_1	B_2	A_1	A_2
B_2	B_2	B_1	A_2	A_1