7 Exercise - Introduction to Group Theory

7.1 (dipole-allowed transitions for benzene located on an unstructured surface)

We start with C_6 symmetry, with the character table:

C_6	E	C_6	C_3	C_2	$(C_3)^2$	$(C_6)^5$	lin fct	quad fct	cub fct
A	1	1	1	1	1	1	z	x^2+y^2, z^2	$z^3, z\left(x^2+y^2\right)$
B	1	-1	1	-1	1	-1	$-$	$-$	$y\left(3x^2-y^2\right), x\left(x^2-3y^2\right)$
E_1	1 1	ε ε^*	$-\varepsilon^*$ $-\varepsilon$	-1 -1	$-\varepsilon$ $-\varepsilon^*$	ε^* ε	$x+iy$ $x-iy$	xz, yz	xz^2, yz^2 $x\left(x^2+y^2\right), y\left(x^2+y^2\right)$
E_2	1 1	$-\varepsilon^*$ $-\varepsilon$	$-\varepsilon$ $-\varepsilon^*$	1 1	$-\varepsilon^*$ $-\varepsilon$	$-\varepsilon$ $-\varepsilon^*$	$-$	x^2-y^2, xy	$xyz, z\left(x^2-y^2\right)$

with $\varepsilon = \exp(2\pi i/6)$ we get:

$$\begin{aligned} \varepsilon + \varepsilon^* &= 2\cos\left(\frac{\pi}{3}\right) = 1 \\ -\varepsilon - \varepsilon^* &= -2\cos\left(\frac{\pi}{3}\right) = -1 \end{aligned}$$

therefore:

C_6	E	C_6	C_3	C_2	$(C_3)^2$	$(C_6)^5$
A	1	1	1	1	1	1
B	1	-1	1	-1	1	-1
E_1	2	1	-1	-2	-1	1
E_2	2	-1	-1	2	-1	-1

We can now have a look at the dipole allowed transitions (at first for the z-component):

total matrix element	finalstate	operator	initial state
A	A	A	A
B	B	A	A
E_1	E_1	A	A
E_2	E_2	A	A
B	A	A	B
A	B	A	B
E_2	E_1	A	B
E_1	E_2	A	B
E_1	A	A	E_1
E_2	B	A	E_1
$2A + E_2$	E_1	A	E_1
$2B + E_1$	E_2	A	E_1
E_2	A	A	E_2
E_1	B	A	E_2
$2B + E_1$	E_1	A	E_2
$2A + E_2$	E_2	A	E_2

now for x, y:

total matrix element	finalstate	operator	initial state
E_1	A	E_1	A
E_2	B	E_1	A
$2A + E_2$	E_1	E_1	A
$2B + E_1$	E_2	E_1	A
E_2	A	E_1	B
E_1	B	E_1	B
$2B + E_1$	E_1	E_1	B
$2A + E_2$	E_2	E_1	B
$2A + E_2$	A	E_1	E_1
$2B + E_1$	B	E_1	E_1
$2B + 3E_1$	E_1	E_1	E_1
$2A + 3E_2$	E_2	E_1	E_1
$2B + E_1$	A	E_1	E_2
$2A + E_2$	B	E_1	E_2
$2A + 3E_2$	E_1	E_1	E_2
$2B + 3E_1$	E_2	E_1	E_2

This means the dipole allowed transitions are:

total matrix element	finalstate	operator	initial state
A	A	A	A
A	B	A	B
$2A + E_2$	E_1	A	E_1
$2A + E_2$	E_2	A	E_2
$2A + E_2$	E_1	E_1	A
$2A + E_2$	E_2	E_1	B
$2A + E_2$	A	E_1	E_1
$2A + 3E_2$	E_2	E_1	E_1
$2A + E_2$	B	E_1	E_2
$2A + 3E_2$	E_1	E_1	E_2

while the first four are no real transitions, while they point to the same orbital. Therefore the only real transitions are:

$$\begin{aligned} E_1 &\leftrightarrow A \\ E_2 &\leftrightarrow B \\ E_1 &\leftrightarrow E_2 \end{aligned}$$

all for E_1, meaning the x, y dipole operator. This leads to the following dipole allowed transitions:

$$\begin{aligned} x, y, xz, yz, xz^2, yz^2, x\left(x^2+y^2\right), y\left(x^2+y^2\right) &\leftrightarrow z, x^2+y^2, z^2, z^3, z\left(x^2+y^2\right) \\ x^2-y^2, xy, xyz, z\left(x^2-y^2\right) &\leftrightarrow y\left(3x^2-y^2\right), x\left(x^2-3y^2\right) \\ x, y, xz, yz, xz^2, yz^2, x\left(x^2+y^2\right), y\left(x^2+y^2\right) &\leftrightarrow x^2-y^2, xy, xyz, z\left(x^2-y^2\right) \end{aligned}$$

7.2 (benzene on Ni(100))

We now place the benzene with C_{6v} on a Nickel surface with C_{4v}. Therefore the symmetry properties will change. We first will try to determine the new point group, which hopefully is C_{2v}, well hopefully we didn't miss a symmetry relation. The character table is given with:

C_{2v}	E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v(yz)$	lin fct	quad fct	cub fct
A_1	1	1	1	1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	1	1	-1	-1	$-$	xy	xyz
B_1	1	-1	1	-1	x	xz	xz^2, x^3, xy^2
B_2	1	-1	-1	1	y	yz	yz^2, y^3, x^2y

We now will try to find all dipole transitions now (z):

total matrix element	finalstate	operator	initial state
A_1	A_1	A_1	A_1
A_2	A_2	A_1	A_1
B_1	B_1	A_1	A_1
B_2	B_2	A_1	A_1
A_2	A_1	A_1	A_2
A_1	A_2	A_1	A_2
B_2	B_1	A_1	A_2
B_1	B_2	A_1	A_2
B_1	A_1	A_1	B_1
B_2	A_2	A_1	B_1
A_1	B_1	A_1	B_1
A_2	B_2	A_1	B_1
B_2	A_1	A_1	B_2
B_1	A_2	A_1	B_2
A_2	B_1	A_1	B_2
A_1	B_2	A_1	B_2

next for (y):

total matrix element	finalstate	operator	initial state
B_2	A_1	B_2	A_1
B_1	A_2	B_2	A_1
A_2	B_1	B_2	A_1
A_1	B_2	B_2	A_1
B_1	A_1	B_2	A_2
B_2	A_2	B_2	A_2
A_1	B_1	B_2	A_2
A_2	B_2	B_2	A_2
A_2	A_1	B_2	B_1
A_1	A_2	B_2	B_1
B_2	B_1	B_2	B_1
B_1	B_2	B_2	B_1
A_1	A_1	B_2	B_2
A_2	A_2	B_2	B_2
B_1	B_1	B_2	B_2
B_2	B_2	B_2	B_2

and at last for (x):

total matrix element	finalstate	operator	initial state
B_1	A_1	B_1	A_1
B_2	A_2	B_1	A_1
A_1	B_1	B_1	A_1
A_2	B_2	B_1	A_1
B_2	A_1	B_1	A_2
B_1	A_2	B_1	A_2
A_2	B_1	B_1	A_2
A_1	B_2	B_1	A_2
A_1	A_1	B_1	B_1
A_2	A_2	B_1	B_1
B_1	B_1	B_1	B_1
B_2	B_2	B_1	B_1
A_2	A_1	B_1	B_2
A_1	A_2	B_1	B_2
B_2	B_1	B_1	B_2
B_1	B_2	B_1	B_2

therefore we this time got the transitions:

total matrix element	finalstate	operator	initial state
A_1	A_1	A_1	A_1
A_1	A_2	A_1	A_2
A_1	B_1	A_1	B_1
A_1	B_2	A_1	B_2
A_1	B_2	B_2	A_1
A_1	B_1	B_2	A_2
A_1	A_2	B_2	B_1
A_1	A_1	B_2	B_2
A_1	B_1	B_1	A_1
A_1	B_2	B_1	A_2
A_1	A_1	B_1	B_1
A_1	A_2	B_1	B_2

This means we got the following transitions:

$$\begin{aligned} B_2 &\leftrightarrow A_1 \text{ for } y \\ B_1 &\leftrightarrow A_2 \text{ for } y \\ B_1 &\leftrightarrow A_1 \text{ for } x \\ B_2 &\leftrightarrow A_2 \text{ for } x \end{aligned}$$

this means in total, the following transitions are possible:

$$\begin{aligned} y, yz, yz^2, y^3, x^2y &\leftrightarrow z, x^2, y^2, z^2, z^3, x^2z, y^2z \\ x, xz, xz^2, x^3, xy^2 &\leftrightarrow xy, xyz \\ x, xz, xz^2, x^3, xy^2 &\leftrightarrow z, x^2, y^2, z^2, z^3, x^2z, y^2z \\ y, yz, yz^2, y^3, x^2y &\leftrightarrow xy, xyz \end{aligned}$$

This means the reduced symmetry leads to more possible transitions compared to task **7.1**.