Direct Products.

Direct Products: The representation of the product of two representations is given by the product of the characters of the two representations.

Verify that under C_{2v} symmetry A2 ⊗ B1 = B2

C_{2v}	E	C_2	σ_v	σ'_v
A_2	1	1	-1	-1
B_1	1	-1	1	-1
$A_2 B_1$	1	-1	-1	1

As can be seen above, the characters of A_2B_1 are those of the B_2 irrep.

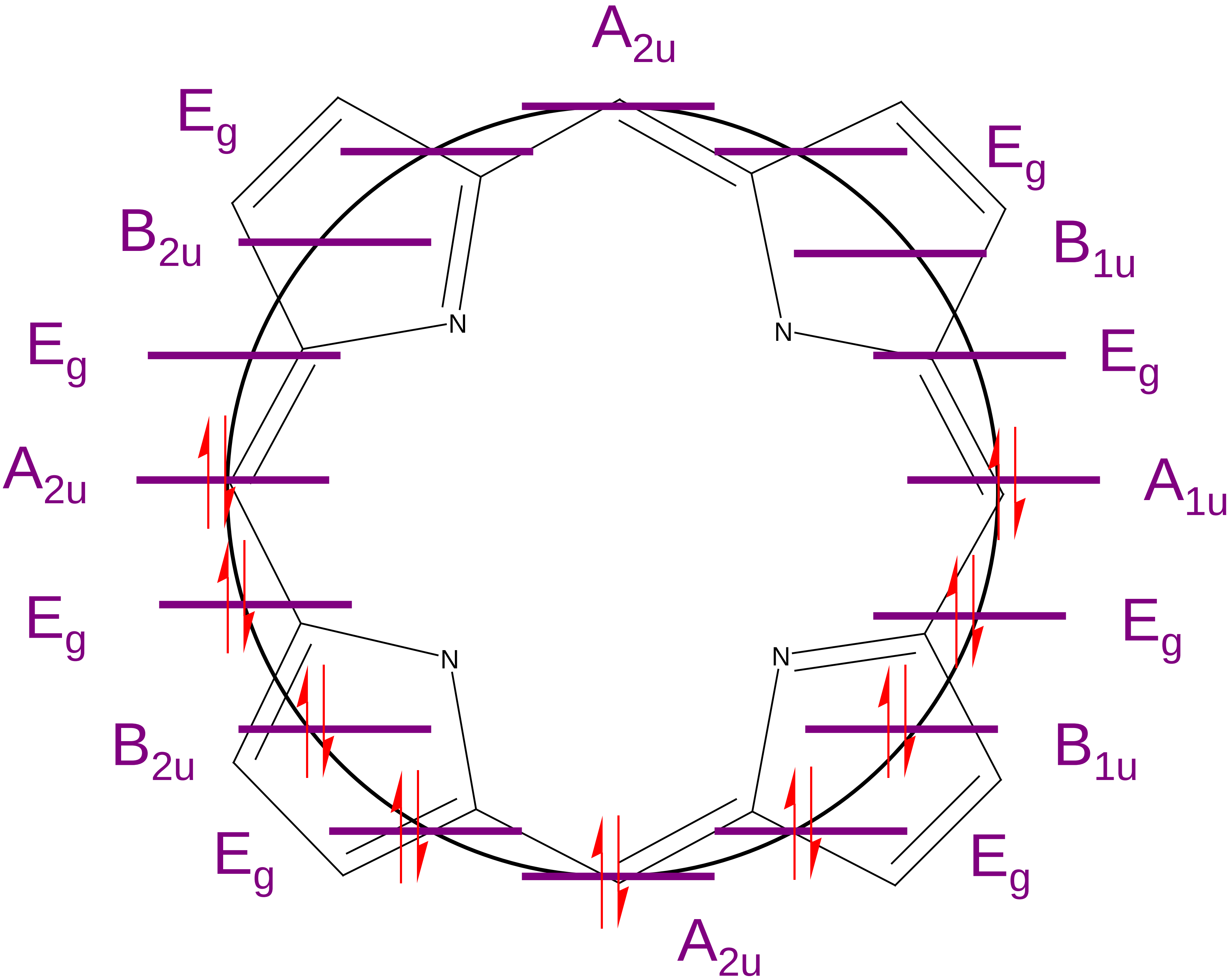
Verify that $A_2 \otimes B_2 = B_1$, $B_2 \otimes B_1 = A_2$

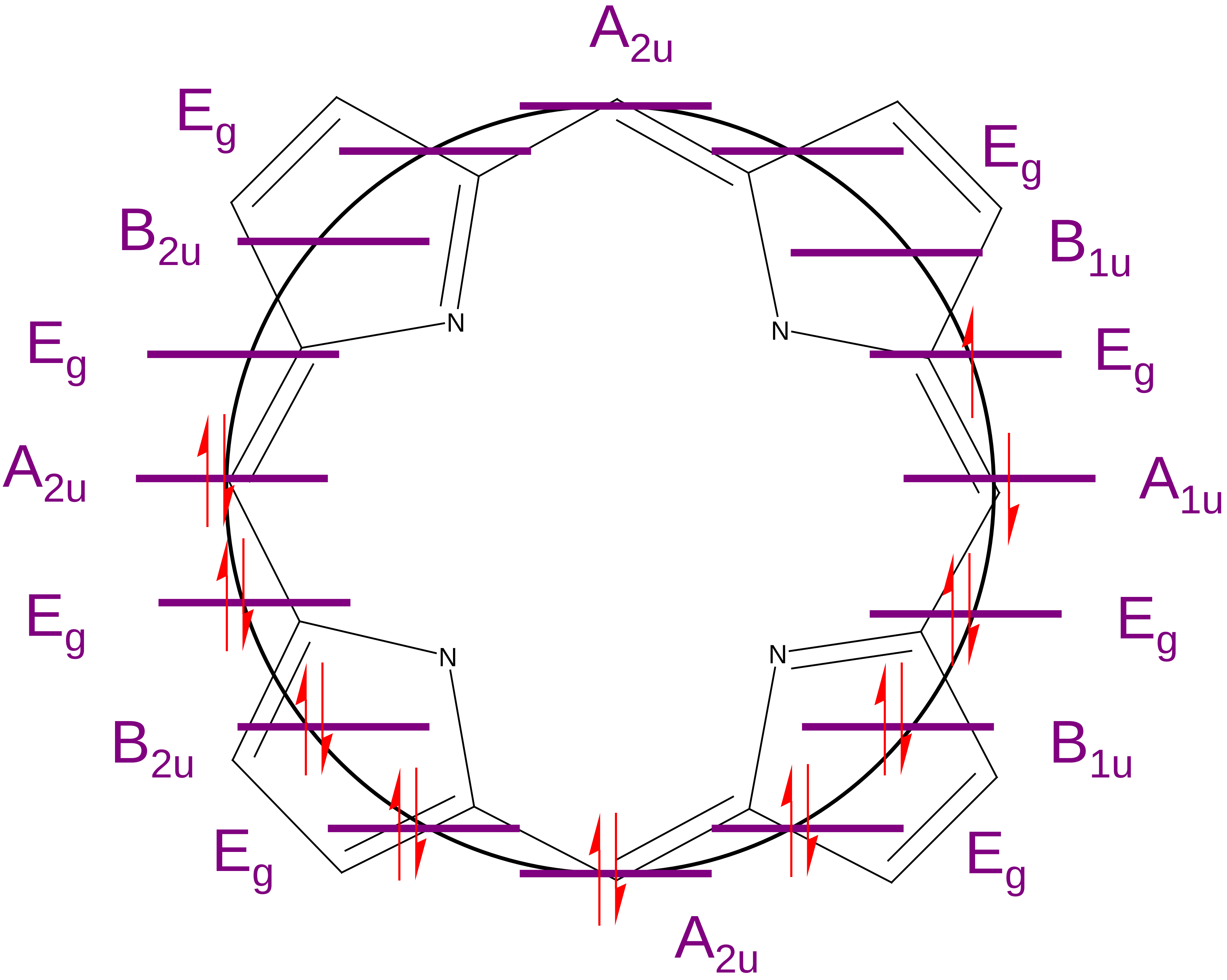
Also verify that

- the product of any non degenerate representation with itself is totally symmetric and
- the product of any representation with the totally symmetric representation yields the original representation

Note that,

- $A \otimes B = B$; while $A \otimes A = B \otimes B = A$
- "1" ⊗ "2" = "2"; while "1" ⊗ "1" = "2" ⊗ "2" = "1"
- $g \otimes u = u$; while $g \otimes g = u \otimes u = g$.


A2u
Eg
Eg
B2u
B1u
Eg
Eg
A2u
A1u
Eg
Eg
B2u
B1u
Eg
Eg
A2u
N
N
N
N


A2u
Eg
Eg
B2u
B1u
Eg
Eg
A2u
A1u
Eg
Eg
B2u
B1u
Eg
Eg
A2u
N
N
N
N

Determining the excited state configuration

The excited state configuration is determined by the direct product of the irreducible representations of each of the molecular orbitals. By definition the configuration of the ground state is $\mathbf{A_{1g}}$. Why?

To obtain the excited state configuration shown in the previous slide we use the product of $A_{1u} \otimes E_g$, which is obtained by multiplying the characters for each will give the symmetry of the excited state configuration.

In the case of porphyrins (and many other aromatic molecules) there are two excited state configurations that can mix by configuration interaction. The requirement for mixing is that the excited state configurations must have the same symmetry.

The excited state configuration for both transitions is the same

The direct product of $A_{1u} \otimes E_g$

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1u}	1	1	1	1	1	-1	-1	-1	-1	-1
E_g	2	0	-2	0	0	2	0	-2	0	0
E_u	2	0	-2	0	0	-2	0	2	0	0

The direct product of $A_{2u} \otimes E_g$

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{2u}	1	1	1	-1	-1	-1	-1	-1	1	1
E_g	2	0	-2	0	0	2	0	-2	0	0
E_u	2	0	-2	0	0	-2	0	2	0	0

Configuration interaction direct product

The direct product of E_u E_u

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
E_u	2	0	-2	0	0	-2	0	2	0	0
E_u	2	0	-2	0	0	-2	0	2	0	0
Γ	4	0	4	0	0	4	0	4	0	0

The decomposition of the product

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
Γ	4	0	4	0	0	4	0	4	0	0
	4	0	4	0	0	4	0	4	0	0 = 16

$$\Gamma(A_{1g}) = 16/16 = 1$$

The decomposition of the product

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
A_{2g}	1	1	1	-1	-1	1	1	1	-1	-1	
Γ	4	0	4	0	0	4	0	4	0	0	
	4	0	4	0	0	4	0	4	0	0	= 16

$$\Gamma(A_{2g}) = 16/16 = 1$$

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
B_{1g}	1	-1	1	1	-1	1	-1	1	1	-1	
Γ	4	0	4	0	0	4	0	4	0	0	
	4	0	4	0	0	4	0	4	0	0	= 16

$$\Gamma(B_{1g}) = 16/16 = 1$$

The decomposition of the product

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
B_{2g}	1	-1	1	-1	1	1	-1	1	-1	1	
Γ	4	0	4	0	0	4	0	4	0	0	
	4	0	4	0	0	4	0	4	0	0	= 16

$$\Gamma(B_{2g}) = 16/16 = 1$$

	E	$2C_4$	C_2	$2C'_2$	$2C''_2$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$	
E_g	2	0	-2	0	0	2	0	-2	0	0	
Γ	4	0	4	0	0	4	0	4	0	0	
	8	0	-8	0	0	8	0	-8	0	0	= 0

$$\Gamma(E_g) = 0$$

The significance of excited state mixing

We have determined that the irreducible representations That promote mixing of the direct product $E_u \otimes E_u$ is given by:

$$\Gamma = A_{1g} + A_{2g} + B_{1g} + B_{2g}$$

Thus, these are the symmetries of the vibrational normal modes that give rise to vibronic coupling.

Of course, the A_{1g} modes are also Franck-Condon active. Thus, we usually consider this activity to be dominant.

It is important to understand that the Fe d-orbitals can also play a role in charge transfer bands or mixing into the $\pi-\pi^*$ transitions of the heme.

Product tables

There are product tables available for each point group. These are posted with character tables. These tables greatly facilitate the task of search for vibronic modes or working through multiple steps that involve configuration interaction.

The product table for D_{4h} on the next page confirms our analysis. We find that $E_u \otimes E_u = A_{1g} + B_{1g} + A_{2g} + B_{2g}$.

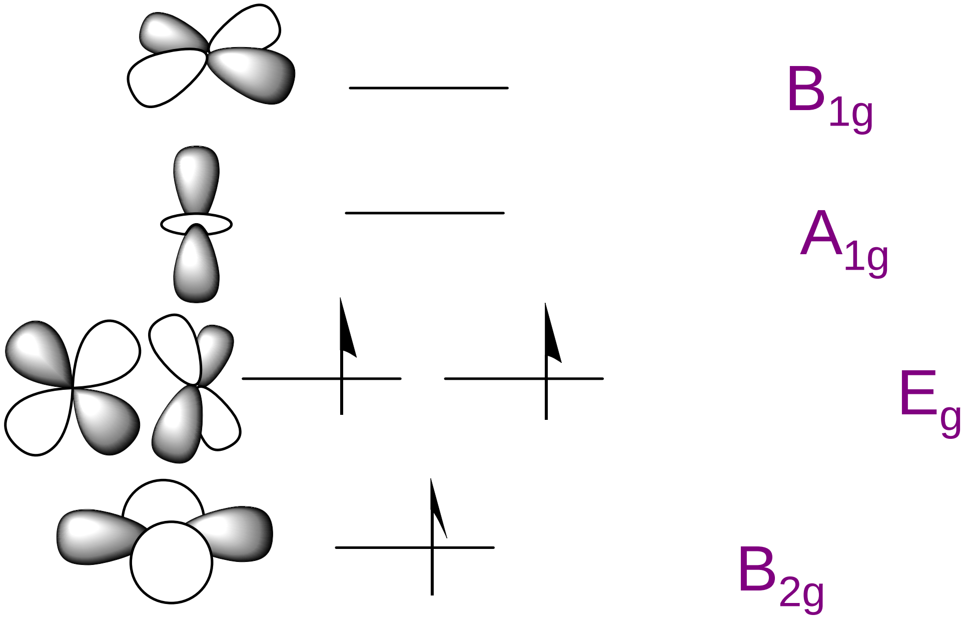
We can show the power of this table by considering the interaction of a metal ion with the orbitals on the porphyrin. If we consider Fe(III) high spin then there are five unpaired electrons. This implies the following direct product on the metal itself $B_{2g} \otimes E_g \otimes E_g \otimes A_{1g} \otimes B_{1g} = B_{2g} \otimes B_{1g} = A_{2g}$
If the porphyrin is in its closed shell ground state, then all electrons are spin paired. The overall configuration is A_{2g}.

Product table for D_{4h}

	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
A_{1g}	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u
A_{2g}	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_g	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_u
B_{1g}	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_g	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_u
B_{2g}	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_g	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_u
E_g	E_g	E_g	E_g	E_g	$A_{1g}+A_{2g}+B_{1g}+B_{2g}$	E_u	E_u	E_u	E_u	$A_{1u}+A_{2u}+B_{1u}+B_{2u}$
A_{1u}	A_{1u}	A_{2u}	B_{1u}	B_{2u}	E_u	A_{1g}	A_{2g}	B_{1g}	B_{2g}	E_g
A_{2u}	A_{2u}	A_{1u}	B_{2u}	B_{1u}	E_u	A_{2g}	A_{1g}	B_{2g}	B_{1g}	E_g
B_{1u}	B_{1u}	B_{2u}	A_{1u}	A_{2u}	E_u	B_{1g}	B_{2g}	A_{1g}	A_{2g}	E_g
B_{2u}	B_{2u}	B_{1u}	A_{2u}	A_{1u}	E_u	B_{2g}	B_{1g}	A_{2g}	A_{1g}	E_g
E_u	E_u	E_u	E_u	E_u	$A_{1u}+A_{2u}+B_{1u}+B_{2u}$	E_g	E_g	E_g	E_g	$A_{1g}+A_{2g}+B_{1g}+B_{2g}$

Irreducible representations of the Fe d-orbitals

S = 5/2



B_{1g}

A_{1g}

E_g

B_{2g}

High spin Fe(III)

Using a product table to predict MLCT

Given this initial configuration we can use the product table To predict which metal-to-ligand charge transfer (MLCT) bands are possible. There are five electrons from the metal (four unique electrons) that could be transferred to the π^* e_g orbital on the porphyrin ring. An allowed transition should have the following characteristic:

$$\Gamma_g \otimes \Gamma_e = \Gamma_{xyz}$$

From the D_{4h} character table we see that A_{2u} and E_u transform as z and x,y, respectively. Thus, our question Is whether any of the electrons give rise to an excited state configuration that makes this possible. The excited state configuration will need to be calculated for 5 electrons and then compared with Γ_{xyz}. One thing that makes this easy is the fact that all of the orbitals involved are gerade. Thus, the transition is not possible since $g \otimes g = g$.

Using a product table to predict LMCT

The ligand to metal involves A_{2u} or A_{1u} to one of the d-orbitals. That is at least possible since $g \otimes u = u$.

$$\Gamma_g \otimes \Gamma_e = \Gamma_{xyz}$$

Thus, we consider
$A_{2u} \rightarrow B_{2g}$: Fe configuration = B_{2g} and $\Gamma_e = A_{2u} \otimes B_{2g} = B_{1u}$
$\Gamma_g \otimes \Gamma_e = B_{2g} \otimes B_{1u} = A_{2u} = \Gamma_z$.
This one is possible as a z-polarized transition

One can continue in this way. When the transition is not allowed then one can search for vibronic modes that could give rise to coupling. One can begin to see the need for the product table. This search can become tedious even with the product table. Without it you might just give up.