Heiko Dumlich 21. November 2007

4 Exercise - Introduction to Group Theory

4.1 (vibrational selection rules)

To find vibrational selection rules, we have to determine whether integrals of the types $\int \psi_\nu^0 \, f \, \psi_\nu^1$ are non-zero, with function f being $x, y, z, x^2, y^2, z^2, xy, yz, zx$ or any combination thereof. Let ψ_ν^0 be totally symmetric and ψ_ν^1 may belong to any irreducible representation. We are now meant to identify the irreducible representations to which ψ_ν^1 may belong in order to give non-zero integrals for molecules of symmetry C_{4v} and D_{3d}. We start out first denoting the character tables of C_{4v}:

C_{4v}	E	$2C_4\,(z)$	C_2	$2\sigma_v$	$2\sigma_d$	linear fcts, rotations	quadratic fcts	cubic functions
A_1	1	1	1	1	1	z	x^2+y^2, z^2	$z^3, z\left(x^2+y^2\right)$
A_2	1	1	1	-1	-1	R_z	$-$	$-$
B_1	1	-1	1	1	-1	$-$	x^2-y^2	$z\left(x^2-y^2\right)$
B_2	1	-1	1	-1	1	$-$	xy	xyz
E	2	0	-2	0	0	$(x,y)\,(R_x,R_y)$	(xz,yz)	$\left(xz^2,yz^2\right)\left(xy^2,x^2y\right)\left(x^3,y^3\right)$

We first start calculating all possible direct products:

$$
\begin{aligned}
A_1 \otimes A_1 &= A_1 \\
A_1 \otimes A_2 &= A_2 \\
A_1 \otimes B_1 &= B_1 \\
A_1 \otimes B_2 &= B_2 \\
A_1 \otimes E &= E
\end{aligned}
$$

further:

$$
\begin{aligned}
E \otimes A_1 &= E \\
E \otimes A_2 &= E \\
E \otimes B_1 &= E \\
E \otimes B_2 &= E \\
E \otimes E &= A_1 + A_2 + B_1 + B_2
\end{aligned}
$$

going on with:

$$
\begin{aligned}
B_1 \otimes A_1 &= B_1 \\
B_1 \otimes A_2 &= B_2 \\
B_1 \otimes B_1 &= A_1 \\
B_1 \otimes B_2 &= A_2 \\
B_1 \otimes E &= E
\end{aligned}
$$

and

$$\begin{aligned}
B_2 \otimes A_1 &= B_2 \\
B_2 \otimes A_2 &= B_1 \\
B_2 \otimes B_1 &= A_2 \\
B_2 \otimes B_2 &= A_1 \\
B_2 \otimes E &= E
\end{aligned}$$

at last

$$\begin{aligned}
A_2 \otimes A_1 &= A_2 \\
A_2 \otimes A_2 &= A_1 \\
A_2 \otimes B_1 &= B_2 \\
A_2 \otimes B_2 &= B_1 \\
A_2 \otimes E &= E
\end{aligned}$$

Therefore $A_1$and E symmetry vibrations will be IR active and A_1, B_1, B_2 and E symmetry vibrations will be Raman active. We used that the direct product should contain the irreducible representation of the irr. rep. we have looked at for the transition.

Now we denote the charater table of D_{3d}:

D_{3d}	E	$2C_3$	$3C_2'$	i	$2S_6$	$3\sigma_d$	linears, rots	quadratics	cubic functions
A_{1g}	1	1	1	1	1	1	$-$	x^2+y^2, z^2	$-$
A_{2g}	1	1	-1	1	1	-1	R_z	$-$	$-$
E_g	2	-1	0	2	-1	0	(R_x, R_y)	$\left(x^2-y^2, xy\right)(xz, yz)$	$-$
A_{1u}	1	1	1	-1	-1	-1	$-$	$-$	$x\left(x^2-3y^2\right)$
A_{2u}	1	1	-1	-1	-1	1	z	$-$	$y\left(x^2-3y^2\right), z^3, z\left(x^2+y^2\right)$
E_u	2	-1	0	-2	1	0	(x, y)	$-$	$\left(xz^2, yz^2\right)\left[xyz, z\left(x^2-y^2\right)\right]$ $\left[x\left(x^2+y^2\right), y\left(x^2+y^2\right)\right]$

We can again calculate all possible direct products:

$$\begin{aligned}
A_{1g} \otimes A_{1g} &= A_{1g} \\
A_{1g} \otimes A_{2g} &= A_{2g} \\
A_{1g} \otimes E_g &= E_g \\
A_{1g} \otimes A_{1u} &= A_{1u} \\
A_{1g} \otimes A_{2u} &= A_{2u} \\
A_{1g} \otimes E_u &= E_u
\end{aligned}$$

next

$$\begin{aligned}
A_{2g} \otimes A_{1g} &= A_{2g} \\
A_{2g} \otimes A_{2g} &= A_{1g}
\end{aligned}$$

$$\begin{aligned}
A_{2g} \otimes E_g &= E_g \\
A_{2g} \otimes A_{1u} &= A_{2u} \\
A_{2g} \otimes A_{2u} &= A_{1u} \\
A_{2g} \otimes E_u &= E_u
\end{aligned}$$

last g

$$\begin{aligned}
E_g \otimes A_{1g} &= E_g \\
E_g \otimes A_{2g} &= E_g \\
E_g \otimes E_g &= A_{1g} + A_{2g} + E_g \\
E_g \otimes A_{1u} &= E_u \\
E_g \otimes A_{2u} &= E_u \\
E_g \otimes E_u &= A_{1u} + A_{2u} + E_u
\end{aligned}$$

now the u-terms:

$$\begin{aligned}
A_{1u} \otimes A_{1g} &= A_{1u} \\
A_{1u} \otimes A_{2g} &= A_{2u} \\
A_{1u} \otimes E_g &= E_u \\
A_{1u} \otimes A_{1u} &= A_{1g} \\
A_{1u} \otimes A_{2u} &= A_{2g} \\
A_{1u} \otimes E_u &= E_g
\end{aligned}$$

next

$$\begin{aligned}
A_{2u} \otimes A_{1g} &= A_{2u} \\
A_{2u} \otimes A_{2g} &= A_{1u} \\
A_{2u} \otimes E_g &= E_u \\
A_{2u} \otimes A_{1u} &= A_{2g} \\
A_{2u} \otimes A_{2u} &= A_{1g} \\
A_{2u} \otimes E_u &= E_g
\end{aligned}$$

last u-term:

$$\begin{aligned}
E_u \otimes A_{1g} &= E_u \\
E_u \otimes A_{2g} &= E_u \\
E_u \otimes E_g &= A_{1u} + A_{2u} + E_u \\
E_u \otimes A_{1u} &= E_g \\
E_u \otimes A_{2u} &= E_g \\
E_u \otimes E_u &= A_{1g} + A_{2g} + E_g
\end{aligned}$$

A_{2u} and E_u symmetry vibrations will be IR active. A_{1g} and E_g symmetry vibrations will be Raman active.

4.2 (magnetic dipole allowed transitions for T_d-symmetry)

For a molecule of T_d symmetry we can determine what pairs of states could be connected by a magnetic dipole allowed transition, while for example Methane got T_d symmetry. The character table of T_d:

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	linears, rots	quadratic fcts	cubic functions
A_1	1	1	1	1	1	$-$	$x^2+y^2+z^2$	xyz
A_2	1	1	1	-1	-1	$-$	$-$	$-$
E	2	-1	2	0	0	$-$	$\left(2z^2-x^2-y^2, x^2-y^2\right)$	$-$
T_1	3	0	-1	1	-1	(R_x, R_y, R_z)	$-$	$\left[x\left(z^2-y^2\right), y\left(z^2-x^2\right), z\left(x^2-y^2\right)\right]$
T_2	3	0	-1	-1	1	(x, y, z)	(xy, xz, yz)	$\left(x^3, y^3, z^3\right)$ $\left[x\left(z^2+y^2\right), y\left(z^2+x^2\right), z\left(x^2+y^2\right)\right]$

The direct products are:

$$
\begin{aligned}
T_1 \otimes A_1 &= T_1 \\
T_1 \otimes A_2 &= T_2 \\
T_1 \otimes E &= T_1 + T_2 \\
T_1 \otimes T_1 &= A_1 + E + T_1 + T_2 \\
T_1 \otimes T_2 &= A_1 + E + T_1 + T_2
\end{aligned}
$$

therefore the following transitions are magnetic dipole allowed:

$$
\begin{aligned}
T_1 &\rightarrow A_1 \\
T_1 &\rightarrow E \\
T_1 &\rightarrow T_1 \\
T_1 &\rightarrow T_2
\end{aligned}
$$

this follows from the condition, that we need to have at least one T_1 in the direct product-reduced form, for the integral not to vanish.