Self-Study / Tutorial / Exam Preparation Problems

- show that the A_1 and A_2 IRs of the C_{3v} point group are orthonormal

C_{3v}	E	$2C_3$	$3\sigma_v$	C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1	A_2	1	1	−1
A_2	1	1	−1	A_2	1	1	−1
$A_1 \otimes A_2$	1	1	−1	$A_2 \otimes A_2$	1	1	1

$$= \frac{1}{6}\sum components\left\{A_1 \otimes A_2\right\} \qquad = \frac{1}{6}\sum components\left\{A_2 \otimes A_2\right\}$$

$$[\underbrace{(1 \bullet 1)}_{E} + \underbrace{(2 \bullet 1)}_{C_3} + \underbrace{(3 \bullet -1)}_{\sigma_v}] = 0 \qquad [\underbrace{(1 \bullet 1)}_{E} + \underbrace{(2 \bullet 1)}_{C_3} + \underbrace{(3 \bullet 1)}_{\sigma_v}] = 1$$

- show that the irreducible representations of the point group C_3 are orthonormal (hint, don't forget that ε^* is the complex conjugate!)

C_3	E	C_3^1	C_3^2
A_1	1	1	1
E	1	ε	ε^*
	1	ε^*	ε

$\varepsilon = \exp(2\pi i/3)$

A and A

$$\frac{1}{3}\left[(1 \bullet 1) + (1 \bullet 1) + (1 \bullet 1)\right] = \frac{1}{3}\left[1 + 1 + 1\right] = \frac{3}{3} = 1$$

A and E

$$\frac{1}{3}\left[(1 \bullet 1) + (1 \bullet \varepsilon) + (1 \bullet \varepsilon^*)\right] = \frac{1}{3}\left[1 + e^{2\pi i/3} + e^{-2\pi i/3}\right] = \frac{1}{3}\left[1 - 1\right] = 0$$

$$e^{i\theta} = \cos\theta + i\sin\theta$$

$$e^{2\pi i/3} = \cos(\frac{2\pi}{3}) + i\sin(\frac{2\pi}{3})$$

$$e^{-2\pi i/3} = \cos(\frac{2\pi}{3}) - i\sin(\frac{2\pi}{3})$$

$$e^{2\pi i/3} + e^{-2\pi i/3} = 2\cos(\frac{2\pi}{3}) = 2\cos(120^\circ) = 2 \bullet -0.5 = -1$$

E and E

$$\frac{1}{3}\left[(1 \bullet 1) + (\varepsilon \bullet \varepsilon^*) + (\varepsilon^* \bullet \varepsilon)\right] = \frac{1}{3}\left[1 + 1 + 1\right] = \frac{3}{3} = 1$$

$$\varepsilon \bullet \varepsilon^* = e^{2\pi i/3} \bullet e^{-2\pi i/3} = e^0 = 1$$

- form the direct product $A_2 \otimes B_2 \otimes B_1$ for the C_{2v} point group
  - using a character table $A_2 \otimes B_2 = B_1$ and $B_1 \otimes B_1 = A_1$

C_{2v}	E	C_2	σ_v	σ_v'
A_2	1	1	−1	−1
B_2	1	−1	−1	1
$A_2 \otimes B_2$	1	−1	1	$-1 \Rightarrow B_1$

  - using the crib sheet $A \otimes B = B$ and $2 \otimes 2 = 1$ so $A_2 \otimes B_2 = B_1$, then $B_1 \otimes B_1 = A_1$ since $B \otimes B = A$ and $1 \otimes 1 = 1$
- determine the irreducible representations spanned by $(x, y, z)^2$ under the C_{3v} point group

$$(x,y) \Rightarrow E \quad z \Rightarrow A_1$$
$$(x,y,z) \Rightarrow E + A_1$$
$$(x,y,z)^2 \Rightarrow (A_1 + E) \otimes (A_1 + E)$$
$$A_1 \otimes A_1 = A_1 \quad A_1 \otimes E = E$$
$$E \otimes A_1 = E \quad E \otimes E = A_1 + A_2 + E$$
$$\Rightarrow 2A_1 + A_2 + 3E$$

  - alternatively you could use the character tables

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(z)$	1	1	1
$\Gamma(x,y)$	2	−1	0
$\Gamma(x,y,z)$	3	0	1
$\Gamma(x,y,z)^2$	9	0	1

then use the reduction formula to determine $\Gamma(x,y,z)^2 = 2A_1 + A_2 + 3E$

- form the direct product $E_1 \otimes T_1 \otimes T_2$ for the tetrahedral point group

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1
$E \otimes T_1 \otimes T_2$	18	0	2	0	0

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
$E\otimes T_1\otimes T_2$	18	0	2	0	0	
A_1	1	1	1	1	1	$\Rightarrow n_{A_1} = \frac{1}{24}\left[(1\bullet 18\bullet 1)+0+(3\bullet 2\bullet 1)\right] = \frac{24}{24} = 1$
A_2	1	1	1	-1	-1	$\Rightarrow n_{A_2} = \frac{1}{24}\left[(1\bullet 18\bullet 1)+0+(3\bullet 2\bullet 1)\right] = \frac{24}{24} = 1$
E	2	-1	2	0	0	$\Rightarrow n_{A_2} = \frac{1}{24}\left[(1\bullet 18\bullet 2)+0+(3\bullet 2\bullet 1)\right] = \frac{42}{24} = 2$
T_1	3	0	-1	1	-1	$\Rightarrow n_{A_2} = \frac{1}{24}\left[(1\bullet 18\bullet 3)+0+(3\bullet 2\bullet -1)\right] = \frac{48}{24} = 2$
T_1	3	0	-1	-1	1	$\Rightarrow n_{A_2} = \frac{1}{24}\left[(1\bullet 18\bullet 3)+0+(3\bullet 2\bullet -1)\right] = \frac{48}{24} = 2$

$$E\otimes T_1\otimes T_2 = \left\{A_1 + A_2 + 2E + 2T_1 + 2T_2\right\}$$

- Use the equation given below to identify and show which irreducible representations of the C_{4v} point group relate to modes that are IR active or inactive.

$$A_1 \in \left\{\Gamma^{\langle\chi_f|}\otimes\Gamma^{|\chi_i\rangle}\otimes\Gamma^{\mu}\right\}$$

  - To determine IR active modes the transition dipole moment must be non-zero and this integral is non-zero only when the above relationship holds.
  - Since the ground state is always totally symmetric (A_1 in C_{4v}) this expression can be simplified to $A_1 \in \left\{\Gamma^{|\chi_i\rangle}\otimes\Gamma^{\mu}\right\}$ for each of the x,y,z components of the dipole vector.
  - For the C_{4v} point group the component irreducible representations of the dipole moment vector are A_1 and E.
  - Potential vibrations ie symmetry of the final state are A_1, A_2, B_1, B_2 and E.
  - The cross products of A_1 with the group of IRs A_1, A_2, B_1, B_2 will just regenerate the identical IRs, thus only $A_1\otimes A_1=A_1$ is viable in the first set.
  - The cross products of E with the non-degenerate irreducible representations are all E and thus cannot be IR active.
  - This leaves $E\otimes E=\{A_1+A_2+B_1+B_2\}$ which does contain A_1 and so E is a viable vibration.
  - Therefor A_1+E are IR active and $A_2+B_1+B_2$ are not IR active