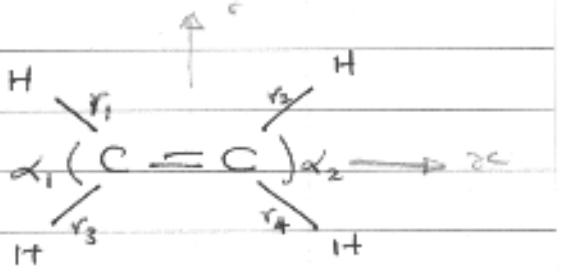
## Second Example

## Symmetry Coordinates for Ethylene

Ethene has a symmetry of $D_{2h}$




For Int = $r_1$

| $D_{2h}$ | $E$ | $C_2(z)$ | $C_2(y)$ | $C_2(x)$ | $i$ | $\sigma(xy)$ | $\sigma(xz)$ | $\sigma(yz)$ | SALCs |
|---|---|---|---|---|---|---|---|---|---|
| $O_R(r_1)$ | $r_1$ | $r_4$ | $r_2$ | $r_3$ | $r_4$ | $r_1$ | $r_3$ | $r_2$ | |
| $A_g$ | 1 | 1 | 1 | 1 | 1 | 1 | 1 | 1 | $2(r_1+r_2+r_3+r_4)$ |
| $B_{1g}$ | 1 | 1 | -1 | -1 | 1 | 1 | -1 | -1 | $2(r_1+r_4-r_2-r_3)$ |
| $B_{2g}$ | 1 | -1 | 1 | -1 | 1 | -1 | 1 | -1 | 0 |
| $B_{3g}$ | 1 | -1 | -1 | 1 | 1 | -1 | -1 | 1 | 0 |
| $A_u$ | | | | | | | | | 0 |
| $B_{1u}$ | | | | | | | | | 0 |
| $B_{2u}$ | 1 | -1 | 1 | -1 | -1 | 1 | -1 | 1 | $2(r_1+r_2-r_3-r_4)$ |
| $B_{3u}$ | 1 | -1 | -1 | 1 | -1 | 1 | 1 | -1 | $2(r_1+r_3-r_2-r_4)$ |

Applying the method on $r_2$, $r_3$ and $r_4$ internal coordinates will result with other sets of SALCs. However, the resultant symmetry coordinates will be eventually in different.

In other words the other SALCs sets will account for degeneracies in some symmetry modes.

$$S^{A_g} = \underbrace{(2^2+2^2+2^2+2^2)^{-1/2}}_{\eta} \left[2(r_1+r_2+r_3+r_4)\right]$$

$$= \frac{1}{4}\left[2(r_1+r_2+r_3+r_4)\right]$$

$$= \frac{1}{2}(r_1+r_2+r_3+r_4)$$

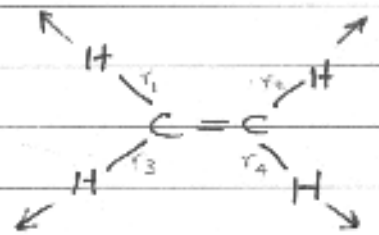
Similarily:

$$S^{B_{1g}} = \frac{1}{2}(r_1+r_4-r_2-r_3)$$

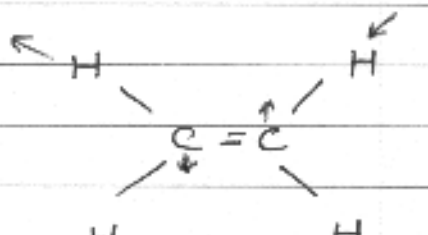
$$S^{B_{2g}} = \frac{1}{2}(r_1+r_2-r_3-r_4)$$

$$S^{B_{3u}} = \frac{1}{2}(r_1+r_3-r_2-r_4)$$

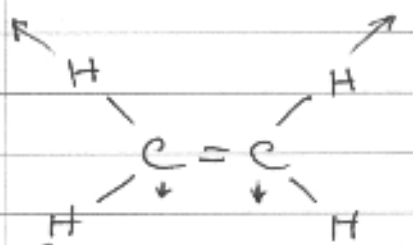
These symmetry coordinates correspond to the vibrations shown below:



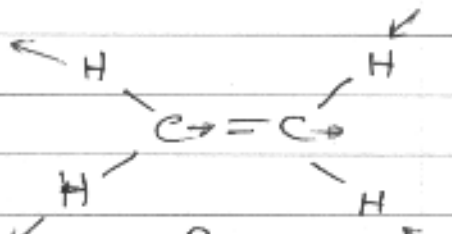

$A_g$




$B_{1g}$




$B_{2g}$




$B_{3u}$

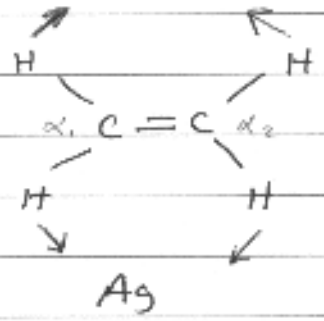
Notice that: carbon atoms move to maintain center of gravity

For Int = $\alpha_1$

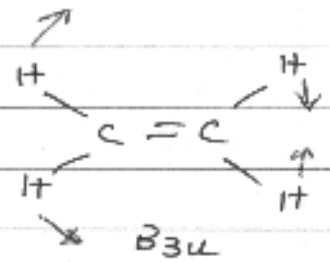
$$S^{A_g} = \frac{1}{\sqrt{2}}(\alpha_1 + \alpha_2)$$

$$S^{B_{3u}} = \frac{1}{\sqrt{2}}(\alpha_1 - \alpha_2)$$

All other symmetry species yield zero



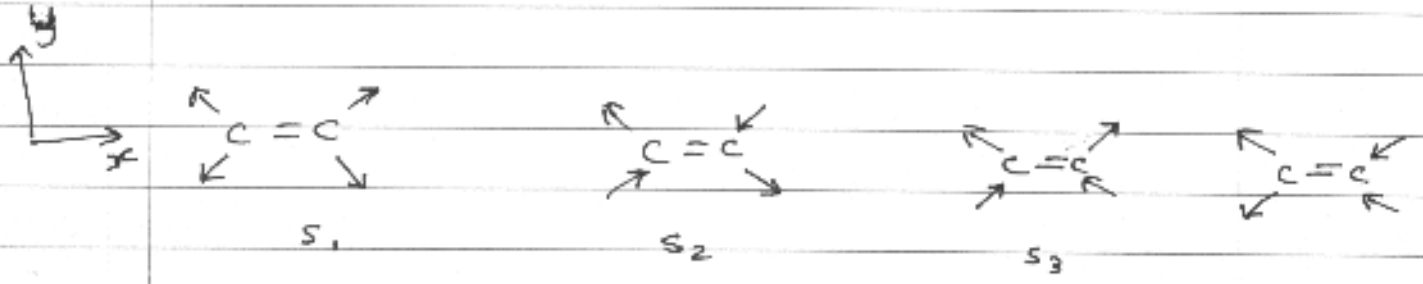

$A_g$




$B_{3u}$

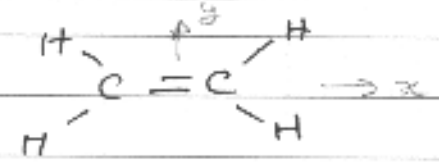
Another technique to identify the symmetry for symmetry coordinates (or vibrations) is the + or − method

This requires you to know the motion prior to apply it.




| $D_{2h}$ | $E$ | $C_2(z)$ | $C_2(y)$ | $C_2(x)$ | $i$ | $\sigma_{xy}$ | $\sigma_{xz}$ | $\sigma_{yz}$ | Sym. |
|---|---|---|---|---|---|---|---|---|---|
| $S_1$ | +1 | +1 | +1 | +1 | +1 | +1 | +1 | +1 | $\Rightarrow A_g$ |
| $S_2$ | +1 | +1 | −1 | −1 | +1 | +1 | −1 | −1 | $\Rightarrow B_{1g}$ |
| $S_3$ | +1 | −1 | +1 | −1 | −1 | +1 | −1 | +1 | $\Rightarrow B_{2u}$ |
| $S_4$ | +1 | −1 | −1 | +1 | −1 | +1 | +1 | −1 | $\Rightarrow B_{3u}$ |

## Determining the Irreducible Representations for the Ethylene Molecule




Ethylene has $D_{2h}$ point group symmetry

| $D_{2h}$ | $E$ | $C_2(z)$ | $C_2(y)$ | $C_2(x)$ | $i$ | $\sigma(xy)$ | $\sigma(xz)$ | $\sigma(yz)$ |
|---|---|---|---|---|---|---|---|---|
| Unshifted atom | 6 | 0 | 0 | 2 | 0 | 6 | 2 | 0 |
| Contribution per atom | 3 | -1 | -1 | -1 | -3 | 1 | 1 | 1 |
| $\Gamma$ | 18 | 0 | 0 | -2 | 0 | 6 | 2 | 0 |

$$\eta^{A_g} = \frac{1}{8}\left[(1\cdot 18\cdot 1) + 0 + 0 + (1\cdot -2\cdot 1) + 0 + (1\cdot 6\cdot 1) + (1\cdot 2\cdot 1) + 0\right]$$

$$= \frac{24}{8} = 3$$

$$\eta^{B_{1g}} = \frac{1}{8}\left[(1\cdot 18\cdot 1) + 0 + 0 + (-1\cdot -2\cdot 1) + 0 + (1\cdot 6\cdot 1) + (-1\cdot 2\cdot 1) + 0\right]$$

$$= \frac{24}{8} = 3$$

$$\eta^{B_{2g}} = \frac{1}{8}\left[(1\cdot 18\cdot 1) + 0 + 0 + (-1\cdot -2\cdot 1) + 0 + (-1\cdot 6\cdot 1) + (1\cdot 2\cdot 1) + 0\right]$$

$$= \frac{16}{8} = 2$$

$$\eta^{B_{3g}} = \frac{1}{8}(18 - 2 - 6 - 2) = \frac{8}{8} = 1$$

$$\eta^{A_u} = \frac{1}{8}(18 - 2 - 6 + 2) = \frac{12}{8} = 1$$

$$\eta^{B_{1u}} = \frac{1}{8}(18 + 2 - 6 + 2) = \frac{16}{8} = 2 \quad ; \quad \eta^{B_{2u}} = \frac{1}{8}(18 + 2 + 6 - 2) = 3$$

$$\eta^{B_{3u}} = \frac{1}{8}(18 - 2 + 6 + 2) = 3$$

$$\Gamma_{tot} = 3A_g + 3B_{1g} + 2B_{2g} + B_{3g} + A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}$$

$$\Gamma_{vib} = \Gamma_{tot} - \Gamma_{trans} - \Gamma_{rot}$$

$$= \Gamma_{tot} - (B_{1u} + B_{2u} + B_{3u}) - (B_{1g} + B_{2g} + B_{3g})$$

$$\Gamma_{vib} = 3A_g + 2B_{1g} + B_{2g} + A_u + B_{1u} + 2B_{2u} + 2B_{3u}$$