

Equivalence (“atomic site”) representation ( $G_{eq}$ ) is formed by vibrational displacements of all atoms consistent with the symmetry operations of the group.

In general,  $G_{eq}$  is reducible. Expand  $G_{eq}$  over irreps.

$$C_{2v} : G_{eq} = a_1 A_1 + a_2 A_2 + a_3 B_1 + a_4 B_2$$

Some of the coefficients should be zero.

Consider rotation by angle  $\theta$   
about some symmetry axis of the molecule in 3D

$$U_\theta = \begin{pmatrix} \cos \theta & \sin \theta & 0 \\ -\sin \theta & \cos \theta & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

Its character:

$$\chi(U_\theta) = \text{Tr} U_\theta = 1 + 2 \cos \theta$$

If there are  $N_a$  atoms on the same axis,

$$\chi(U_\theta) = N_a(1 + 2 \cos \theta)$$

Each of the  $N_a$  atoms was subjected not only to vibrations but also to translations and rotations  $\Rightarrow$   
 $\chi(U_\theta)$  contains extra degrees of freedom.