2H43 INTRODUCTORY THEORETICAL CHEMISTRY

Molecular symmetry and Group Theory

3 Lectures by Dr S. H. Ashworth.

IMPORTANT RESULTS

Properties of a group:

1. There is a rule to combine two members of a group: known as "multiplication".
2. The "multiplication" must be associative: $(AB)C = A(BC)$
3. The group contains an identity element E.
4. For every element there is an inverse such that: $AA^{-1} = A^{-1}A = E$

Order of a group:

Usually denoted h is the number of symmetry *operations* in a group.

Symmetry elements and operations

Symmetry elements		Symmetry operation	
Symbol	Description	Symbol	Description
E	Identity	$\hat{E}$	No change
C_n	n-fold axis of symmetry	$\hat{C}_n$	Rotation about axis by $(360/n)^o$
σ	Plane of symmetry	$\hat{\sigma}$	Reflection through the plane
i	Centre of symmetry	$\hat{1}$	Reflection through the centre
S_n	Improper rotation (n-fold rotation reflection)	$\hat{S}_n$	Rotation around axis by $(360/n)^o$ followed by reflection through a plane perpendicular to the axis

Notation

- Γ The representation of a point group which can either be reducible or written as a linear combination of irreducible representations.
- $\hat{R}$ A general symmetry operation. In an equation this will be substituted by all the symmetry operations of a point group, one after another. (This distinguishes between C_3 and C_3^2.)
- $\chi\left(\hat{R}\right)$ The character of symmetry operation $\hat{R}$.

Some mathematical relationships

$$\sum_{j=1}^{N} d_j^2 = \sum_{j=1}^{N} [\chi_j(\hat{E})]^2 = h \qquad (1.1)$$

Where N is the number of symmetry ***operations***.

We know that the dot product of two vectors can be written:

$$\mathbf{u} \cdot \mathbf{v} = |u||v| \cos \vartheta = \sum_{k=1}^{n} u_k v_k \tag{1.2}$$

If we think of a row of the character table in terms of an abstract vector we can write:

$$\sum_{\hat{R}} \chi_i(\hat{R}) \chi_j(\hat{R}) = 0 \qquad i \neq j \tag{1.3}$$

This is the same as writing:

$$\sum_{\text{classes}} n(\hat{R}) \chi_i(\hat{R}) \chi_j(\hat{R}) = 0 \qquad i \neq j \tag{1.4}$$

This can be further summarised to:

$$\sum_{\hat{R}} \chi_i(\hat{R}) \chi_j(\hat{R}) = \sum_{\text{classes}} n(\hat{R}) \chi_i(\hat{R}) \chi_j(\hat{R}) = h\delta_{ij} \tag{1.5}$$

where δ_{ij} represents the Kröneker delta.

To reduce an irreducible representation Γ to a linear combination of irreducible representations with coefficients a_i we use the relation:

$$a_i = \frac{1}{h} \sum_{\hat{R}} \chi(\hat{R}) \chi_i(\hat{R}) = \frac{1}{h} \sum_{\text{classes}} n(\hat{R}) \chi(\hat{R}) \chi_i(\hat{R}) \tag{1.6}$$

(For more detail see *Physical Chemistry: a Molecular Approach*, McQuarrie and Simon.)

Infra-red and Raman activity:

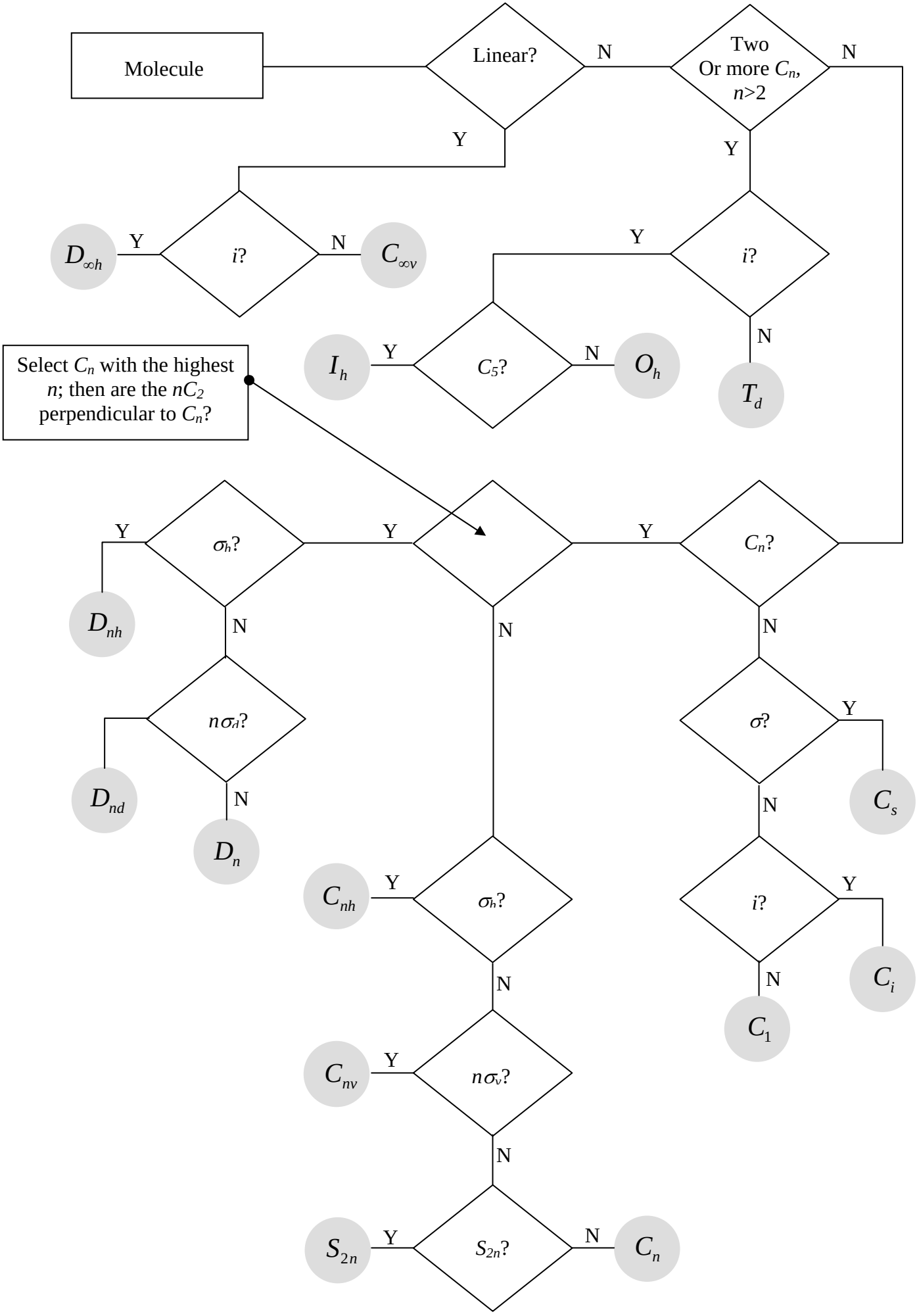
1. Form a reducible representation using *x*, *y*, and *z* matrices on each atom.
2. Express this representation in terms of irreducible representations using Equation (1.6)
3. Discard irreducible representations corresponding to rotations and translations.
4. IR active vibrations transform as the *p*-orbital-like functions. Raman active vibrations transform as the *d*-orbital-like functions.

Allowed electronic transitions:

An electronic transition in a molecule will be allowed when the following condition is fulfilled:

$$\Gamma\left(\Psi_i\right) \times \Gamma\left(\hat{\mu}\right) \times \Gamma\left(\Psi_f\right) \supset A \tag{1.7}$$

Where $\supset$ should be read as "contains" and A is the totally symmetric irreducible representation in the appropriate point group (*e.g.* A_1 in C_{2v})


Molecule
Linear?
N
Two
Or more C_n,
n>2
N
Y
Y
$D_{\infty h}$
Y
i?
N
$C_{\infty v}$
Y
i?
Y
I_h
Y
C_5?
N
O_h
N
T_d
Select C_n with the highest n; then are the nC_2 perpendicular to C_n?
Y
σ_h?
Y
Y
C_n?
D_{nh}
N
N
N
$n\sigma_d$?
σ?
Y
D_{nd}
N
C_s
N
D_n
C_{nh}
Y
σ_h?
i?
Y
N
N
C_i
C_{nv}
Y
$n\sigma_v$?
C_1
N
S_{2n}
Y
S_{2n}?
N
C_n