Physical Chemistry

Lecture 28

Polyatomic Molecules and Symmetry

Structure of polyatomic molecules

- More complex than diatomics
- Wave functions determine structure
  - Structure specifies qualities of the wave function
- Structure and wave functions determined by potential-energy terms
- Schroedinger's equation is difficult to solve
- Focus on labeling energy states

$$H\Psi = E\Psi$$

Symmetry and energy

- If a molecule's electron density has a symmetry property
  - The wave function is an eigenfunction of the operator, O
  - The wave function is also an eigenfunction of H
- Requirement for simultaneous eigenfunctions
  - Operators must commute
- Use eigenvalues of symmetry operators to label energy states

$$O\left(\Psi^*\Psi\right) = \Psi^*\Psi$$

$$O\Psi = \pm 1\Psi$$

$$H\Psi = E\Psi$$

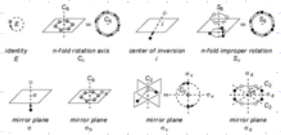
$$[O,H] = 0$$

$$H(O\Psi) = E(O\Psi)$$

Equilibrium structures and point-group symmetry

- Symmetry determined by potential energy
- Energy of equivalent structures must be the same
- Use an eigenvalue approach to describe states
- Symmetry operations that may leave a structure unchanged
  - Identity, E
  - Rotation by $2\pi/n$, C_n
  - Inversion, I
  - Reflection through a plane, σ

$$O\Psi = o\,\Psi$$



Point-group symmetry

- Molecule may have more than one symmetry element
  - Place a molecule in a point group by identifying all unique symmetry elements of the electron density
- A set of elements defines a point group
  - All elements of a point group must have the property that, if the operations A and B are members of the group, so is the product of the operations, AB
- A wide variety of types of groups
  - Restrict focus to groups with operations that
    - Maintain size
    - Rotate structure
    - Reflect structure
    - Invert structure

Point group names

- A group has a name
- Two conventions on naming point groups
  - Hermann-Mauguin system
  - Schoenfliess system
- Schoenfliess system is convenient for spectroscopists
- Hermann-Mauguin more convenient for persons who study point symmetry in conjunction with spatial symmetry

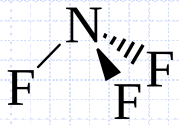
GROUP NAME	SYMMETRY ELEMENTS
(a) Groups with no proper rotation axis	
C_1	E
C_s	E, σ
C_i	E, i
S_n	E, S_n
(b) Groups with one proper rotation axis	
C_n	E, C_n
C_{nv}	E, C_n, n σ_v
C_{nh}	E, C_n, σ_h
(c) Dihedral groups	
D_n	E, C_n, n C_2
D_{nh}	E, C_n, n C_2, σ_h
D_{nd}	E, C_n, n C_2, n σ_d
(d) Linear groups	
$C_{\infty v}$	E, C_∞, $\infty\ \sigma_v$
$D_{\infty h}$	E, C_∞, $\infty\ \sigma_v$, $\infty\ C_2$, σ_h
(e) High-symmetry group	
T_d	Elements of a tetrahedron
O_h	Elements of an octahedron
I_h	Elements of an icosahedron

Determining the point group of a molecule

- Identify all operations that leave the electron density apparently unchanged
- Often taught with a flow-chart method
  - Systematically finds symmetry elements and those that are missing
  - The set of operations corresponds to a particular representation of the group

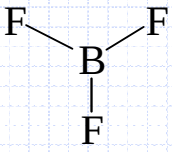
Example: NF_3

- Symmetry elements
  - Identity
  - 2 C_3 rotation axes
    - Positive rotation
    - Negative rotation
  - Three vertical reflection planes
- Compare to point groups
  - Point group of C_{3v}



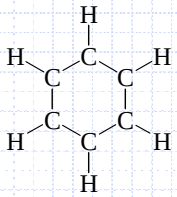
Example: BF_3

- This molecule is planar
- Identify elements
  - Identity
  - 2 C_3 rotation axes
  - One σ_h horizontal reflection plane
  - Three σ_v vertical reflection planes
  - 3 C_2 rotation axes
- Comparison gives point group of D_{3h}



Example: benzene

- Identify elements
  - Identity
  - C_6 rotation axis
  - 6 σ_v reflection planes
  - 6 C_2 axes
  - Because of high symmetry, there are additional elements
- Comparison shows that the point group is D_{6h}



Summary

- Structural symmetry gives a means of labeling energy states
- Point-group theory allows one to classify electronic structure
  - Must identify symmetry elements of molecular electron density
  - Set of elements gives the point group of the electron density
- Two labeling schemes for point groups
  - Schoenfliess notation
  - Hermann-Mauguin notation
  - Generally use Schoenfliess notation when discussing spectroscopy of a single molecule