Lecture 1/11

Fundamentals of Molecular Symmetry

An internet lecture course
Literature:


Contents I:

Symmetry in general.

The symmetry of a molecule.

Groups and point groups.
Irreducible representations, Characters.

The molecular point group.
The CNPI-Group.

The molecular symmetry group (MS group).

Nuclear spin statistical weights, Bose-Einstein/Fermi-Dirac statistics, Pauli principle
Hyperfine structure

Non-rigid molecules: Inversion, internal rotation

Forward and reverse correlation
Contents III:

Vanishing Integral Rule

Selection rules for transitions

Symmetry breakdown?

The classification of molecular states in the MS group:

1) Electronic states
2) Vibrational states
3) Rotational states
Symmetrical, eh?
People build symmetrically......
Natural objects are symmetrical......
And we are symmetrical ourselves.....
(Geometrical) symmetry operations

\[ C_3^2 = \sigma_2 \sigma_1 \]
Geometrical symmetry of H$_2$O

\[ C_{2v} = \{ E, C_2, \sigma_{xy}, \sigma_{yz} \} \]

Multiplication table \((R_{\text{row}} \ R_{\text{column}})\)

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\(C_{2v}\) is a (point) group!
Group axioms

\[ C_{2v} = \{ E, C_2, \sigma_{xy}, \sigma_{yz} \} \]

- All possible products \( RS = T \) belong to the group
- Group contains neutral element \( E \) (which does nothing)
- Each element has inverse element \( R^{-1} \) \((R^{-1}R = RR^{-1} = E)\) in the group
- Associative law \((AB)C = A(BC)\) holds

\[
\begin{array}{c|cccc}
 & E & C_2 & \sigma_{yz} & \sigma_{xy} \\
\hline
E & E & C_2 & \sigma_{yz} & \sigma_{xy} \\
C_2 & C_2 & E & \sigma_{xy} & \sigma_{yz} \\
\sigma_{yz} & \sigma_{yz} & \sigma_{xy} & E & C_2 \\
\sigma_{xy} & \sigma_{xy} & \sigma_{yz} & C_2 & E \\
\end{array}
\]
Molecules have geometrical symmetry - in their equilibrium configurations.
... but what happens to the symmetry when the molecule vibrates?

\[ \text{H}_2\text{O} \]
Symmetry: Formal definition

\( S \) is an operation (operator).

\( H_{rve} \) is the molecular rovibronic Hamiltonian.

\( S \) is a symmetry operation when

\[
[S, H_{rve}] = SH_{rve} - H_{rve}S = 0
\]

i.e., when \( S \) commutes with the Hamiltonian.

What does this have to do with symmetry?
Symmetry types

- Translational symmetry (Uniformity of space).
- Rotational symmetry (Isotropy of space).
- Inversion symmetry (parity, electromagnetic interaction + strong interaction, no property of space).
- Identical particle permutation symmetry (Indistinguishability of identical particles).
- Time reversal symmetry (Electromagnetic forces, no property of space-time).
- (Charge conjugation symmetry)
Rotational symmetry (Isotropy of space).

**FACTORIZATION:**
The Hamiltonian matrix factorizes into blocks for basis functions having common values of $F$ and $m_F$. This reduces the numerical work involved in diagonalizing the matrix.

**LABELING:**
The solutions can be labeled by their values of $F$ and $m_F$ (which are good quantum numbers). With this labeling, it is easier to keep track of the solutions and we can use the good quantum numbers to express selection rules for molecular interactions and transitions.

Electric dipole transitions in field free space take place if and only if

$$|F' - F''| \leq 1 \quad \text{and} \quad F' + F'' \geq 1.$$
Symmetry types

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Permutation-inversion symmetry of H$_2$O

$C_{2v}(M) = \{ E, (12), E^*, (12)^* \}$
Permutation-inversion operations can be multiplied...

\[ C_{2v}(M) = \{ E, (12), E^*, (12)^* \} \]

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\(C_{2v}(M)\) is a (CNPI) group!
Group axioms

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Permutation symmetry example: PH$_3$

The CNP group has 6 elements – but what are the cyclic permutations (123) and (132)?
Transposition

\[(12) \begin{array}{ccc} 1 & 2 & 3 \\ \end{array} = \begin{array}{ccc} 2 & 1 & 3 \\ \end{array}\]

Cyclic permutations

\[(123) \begin{array}{ccc} 1 & 2 & 3 \\ \end{array} = \begin{array}{ccc} 2 & 3 & 1 \\ \end{array}, \quad (132) \begin{array}{ccc} 1 & 2 & 3 \\ \end{array} = \begin{array}{ccc} 3 & 1 & 2 \\ \end{array}\]

\{E, (12), (13), (23), (123), (132)\} are all possible permutations

\[G_{\text{CNPI}} = \{E, (12), (13), (23), (123), (132), E^*, (12)^*, (13)^*, (23)^*, (123)^*, (132)^*\}\] is the CNPI group