Lecture 8/11

Fundamentals of Molecular Symmetry

An internet lecture course
The feasibility of an operation depends on potential energy barriers and experimental resolution.

Should we extend this definition?
\[ E(J_\text{KaKc}) - E(J_{J0}) \]

\[ \begin{align*}
J_{J,0} \\
J_{J,1} \\
J_{J-1,1} \\
J_{J-1,2} \\
J_{J-2,2} \\
J_{J-2,3} \\
J_{J-3,3} \\
J_{J-3,4} \\
J_{J-4,4}
\end{align*} \]

\( A_c = 6.26, \quad B_c = 6.11, \quad C_c = 3.09 \text{ cm}^{-1} \)
Actual H$_2$Te Energy Levels [$E(J_{KaKc}) - E(J_{J0})$]
\[ \Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus B_1 \oplus B_2 \text{ in } C_{2v}(M) \]
Six-fold energy clusters in the vibrational ground state of PH$_3$

$\Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M)$
\[ \Gamma_{\text{Cluster}} = A_1 \oplus A_2 \oplus 2E \quad \text{in } C_{3v}(M) \]
Clusters can be explained by semi-classical theory

\[ \dot{q}_n = \frac{\partial H_{rv}}{\partial p_n}, \]
\[ \dot{p}_n = -\frac{\partial H_{rv}}{\partial q_n}, \]
\[ \dot{J}_\alpha = \{ J_\alpha, H_{rv} \} = 0 \]

\[ J_x = \sqrt{J(J + 1)} \sin \theta_J \cos \phi_J \]
\[ J_y = \sqrt{J(J + 1)} \sin \theta_J \sin \phi_J \]
\[ J_z = \sqrt{J(J + 1)} \cos \theta_J. \]
Rotational energy surface

Classical Hamiltonian function

\[ E_J(\theta_J, \phi_J) = H_{rv}(J, q_n = q^s_n, p_n = p^s_n, \theta_J, \phi_J) \]

\[
\begin{align*}
J_x &= \sqrt{J(J+1)} \sin \theta_J \cos \phi_J \\
J_y &= \sqrt{J(J+1)} \sin \theta_J \sin \phi_J \\
J_z &= \sqrt{J(J+1)} \cos \theta_J .
\end{align*}
\]

The rotational energy surface is a radial plot of \( E_J - E_J^{(\text{min})} \) as a function of \( \theta_J, \phi_J \)
$\text{PH}_3$ rotational energy surface, $J = 100$

Six equivalent maxima

Each cluster state at highest energy corresponds to stable angular momentum trajectory around a maximum

Cluster states are „localized“ at their respective maxima

„No tunneling between cluster states“
Extension of feasibility definition:

Old:

If energy splittings resulting from potential energy tunneling cannot be resolved, permutation-inversion operations accompanied by this tunneling are considered unfeasible.

New = Old together with:

If energy splittings resulting from rotational energy surface tunneling cannot be resolved, permutation-inversion operations accompanied by this tunneling are considered unfeasible.

Application to $H_2X$:

MS group is $C_{2v}(M) = \{ E, (12), E^*, (12)^* \}$

When tunneling between cluster states is neglected, $(12), E^*, (12)^*$ are unfeasible, only $E$ is feasible.

New MS group is $C_1 = \{ E \}$ with one irrep $A$

Reverse correlation $C_1 \rightarrow C_{2v}(M)$

$$A \rightarrow A_1 \oplus A_2 \oplus B_1 \oplus B_2$$
Application to $\text{PH}_3$:

MS group is $C_{3v}(M) = \{ E, (123),(132) , (12)^*,(13)^*,(23)^* \}$

When tunneling between cluster states is neglected, $(123)$, $(132)$, $(12)^*$, $(13)^*$, $(23)^*$ are unfeasible, only $E$ is feasible.

New MS group is $C_1 = \{ E \}$ with one irrep $A$

Reverse correlation $C_1 \rightarrow C_{3v}(M)$

$$A \rightarrow A_1 \oplus A_2 \oplus 2E$$
The MS group of $C_{60}$ is the icosahedral group with 120 elements.
The MS group of the ammonia dimer \((\text{NH}_3)_2\) has 144 elements when the effect of inversion of the two \text{NH}_3 moieties is observable.

Does \((\text{NH}_3)_2\) then have higher symmetry than \(C_{60}\)?
Symmetry and molecules - summary:

- Symmetry operations (e.g., permutation-inversion operations) for a molecule leave the molecular Hamiltonian invariant.

- The operations can be organized in symmetry groups.

- The symmetry groups have irreducible representations.

- The wavefunctions for the molecular eigenstates transform according to the irreducible representations of the symmetry group.
How does symmetry help us?

A. In practice, we solve the molecular Schrödinger by diagonalizing matrix representations of the Hamiltonian. These calculations are facilitated by symmetry.

B. Symmetry imposes selection rules on molecular transitions (for example, absorption and emission transitions).
Vanishing integral rule

The quantum mechanical integral

\[ I = \int \psi''^* \hat{D} \psi'' \, d\tau \]

must vanish (i.e., be = 0) unless the integrand

\[ \psi''^* \hat{D} \psi'' \]

contains a totally symmetric component in the symmetry group(s) of the Hamiltonian.
Parenthetical remark: symmetry of a product

Given two sets of wavefunctions

\[ \Phi_{n1}, \Phi_{n2}, \Phi_{n3}, \Phi_{n4}, \ldots, \Phi_{nr} \quad \text{s-fold degenerate, irrep } \Gamma_n \]

\[ \Phi_{m1}, \Phi_{m2}, \Phi_{m3}, \Phi_{m4}, \ldots, \Phi_{ms} \quad \text{r-fold degenerate, irrep } \Gamma_m \]

Which representation is generated by the set of products \( \Phi_{ni} \Phi_{mj}, \ i = 1, 2, 3, \ldots, s; \ j = 1, 2, 3, \ldots, r \)?
Effect of symmetry operation \( R \) on the functions \( \Phi_{ni} \) and \( \Phi_{mj} \):

\[
R\Phi_{ni} = \sum_{k=1}^{s} D^\Gamma_n [R]_{ik} \Phi_{nk}
\]

\[
R\Phi_{mj} = \sum_{l=1}^{r} D^\Gamma_m [R]_{jl} \Phi_{ml}
\]

Effect of \( R \) on the product \( \Phi_{ni} \Phi_{mj} \):

\[
R[\Phi_{ni} \Phi_{mj}] = \sum_{k=1}^{s} \sum_{l=1}^{r} D^\Gamma_n [R]_{ik} D^\Gamma_m [R]_{jl} \Phi_{nk} \Phi_{ml}
\]
Effect of $R$ on the product $\Phi_{ni} \Phi_{mj}$:

$$R[\Phi_{ni} \Phi_{mj}] = \sum_{k=1}^{s} \sum_{l=1}^{r} D^\Gamma_n [R]_{ik} D^\Gamma_m [R]_{jl} \Phi_{nk} \Phi_{ml}$$

Short-hand notation:

$$R\Psi_{ij} = \sum_{k,l=1,1}^{s,r} D^\Gamma_{nm} [R]_{ij,kl} \Psi_{kl}$$

Elements of transformation „supermatrix“:

$$D^\Gamma_{nm} [R]_{ij,kl} = D^\Gamma_n [R]_{ik} D^\Gamma_m [R]_{jl}$$

Diagonal elements:

$$D^\Gamma_{nm} [R]_{ij,ij} = D^\Gamma_n [R]_{ii} D^\Gamma_m [R]_{jj}$$
Diagonal elements of transformation „supermatrix“:

\[ D^{\Gamma_{nm}} [R]_{i,j,i,j} = D^{\Gamma_n} [R]_{i,i} D^{\Gamma_m} [R]_{j,j} \]

Characters of „product representation“ \( \Gamma_{nm} \):

\[ \chi^{\Gamma_{nm}} [R] = \sum_{i,j=1,1}^{s,r} D^{\Gamma_{nm}} [R]_{i,j,i,j} = \sum_{i,j=1,1}^{s,r} D^{\Gamma_n} [R]_{i,i} D^{\Gamma_m} [R]_{j,j} = \chi^{\Gamma_n} [R] \chi^{\Gamma_m} [R]. \]

Notation (direct product):

\[ \Gamma_{nm} = \Gamma_n \otimes \Gamma_m \]
# Example: $C_{3v}(M)$

<table>
<thead>
<tr>
<th>$C_{3v}(M)$:</th>
<th>$E$</th>
<th>(123)</th>
<th>(23)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$C_{3v}$:</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3\sigma_v$</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>Equiv. rot.:</th>
<th>$R^0$</th>
<th>$R_z 2\pi/3$</th>
<th>$R_\pi/2 \pi$</th>
</tr>
</thead>
</table>

| $A_1$: | 1 | 1 | 1 |
| $A_2$: | 1 | 1 | $-1$ |
| $E$: | 2 | $-1$ | 0 |

**Tensor Product Calculations**

- $A_1 \otimes A_1 = A_1$
- $A_1 \otimes A_2 = A_2$
- $A_2 \otimes A_2 = A_1$
- $A_1 \otimes E = E$
- $A_2 \otimes E = E$
- $E \otimes E = A_1 \oplus A_2 \oplus E$

\[ a_i = \frac{1}{\hbar} \sum_R \chi^\Gamma[R] \chi^{\Gamma_i[R]} [R]^* \]
Special case:

\( \Phi_{n1}, \Phi_{n2} \) have \( E \) symmetry in \( C_{3v}(M) \)

Which representation is generated by the three products \( \Phi_{n1} \Phi_{n1}, \Phi_{n2} \Phi_{n2}, \Phi_{n1} \Phi_{n2} = \Phi_{n2} \Phi_{n1} \) ?

Symmetric product representation:

\[
[E]^2 = [E \otimes E] = A_1 \oplus E
\]

with characters:

\[
\chi^{[E \otimes E]}[R] = \frac{1}{2}((\chi^E[R])^2 + \chi^E[R^2])
\]
Special case:

Characters:

\[ \chi^{E \otimes E}[R] = \frac{1}{2} \left( (\chi^{E}[R])^2 + \chi^{E}[R^2] \right) \]

\[
\begin{align*}
C_{3v}(M): & \quad E & (123) & (23)^* \\
1 & 2 & 3 \\
C_{3v}: & \quad E & 2C_3 & 3\sigma_v \\
\text{Equiv. rot.:} & \quad R^0 & R_z^{2\pi/3} & R_{\pi/2}^\pi \\
A_1: & \quad 1 & 1 & 1 \\
A_2: & \quad 1 & 1 & -1 \\
E: & \quad 2 & -1 & 0 \\
[E \otimes E]: & \quad 3 & 0 & 1 \\
E^2 = E \\
(123)^2 = (132) \\
((12)^*)^2 = E \\
\end{align*}
\]

\[ [E]^2 = [E \otimes E] = A_1 \oplus E \]

\[ a_i = \frac{1}{\hbar} \sum_{R} \chi^\Gamma[R] \chi^{\Gamma_i}[R]^* \]
Antisymmetric product representation:

\[ \{E\}^2 = \{E \otimes E\} = A_2 \]

with characters:

\[ \chi^{\{E \otimes E\}}[R] = \frac{1}{2}((\chi^E[R])^2 - \chi^E[R^2]) \]

<table>
<thead>
<tr>
<th>(C_{3v}(M):)</th>
<th>(E)</th>
<th>(123)</th>
<th>(23)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(C_{3v}:)</th>
<th>(E)</th>
<th>2(C_3)</th>
<th>3(\sigma_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Equiv. rot.}:)</td>
<td>(R^0)</td>
<td>(R_z^{2\pi/3})</td>
<td>(R_{\pi/2})</td>
</tr>
<tr>
<td>(A_1:)</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>(A_2:)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>(E:)</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>({E \otimes E}:)</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

\[ a_i = \frac{1}{h} \sum_R \chi^\Gamma[R] \chi^\Gamma_i[R]^* \]
$n$th order symmetric product representation $[\mathcal{E}]^n$

has the characters

$$
\chi^{[\mathcal{E}]^n}[R] = \frac{1}{2}\left(\chi^E[R]\chi^{[\mathcal{E}]^{n-1}}[R] + \chi^E[R^n]\right)
$$

Its dimension is $n + 1$ and it is generated, for example, by the $n + 1$ products:

$$
\Phi_{n1}^n, \Phi_{n1}^{n-1}\Phi_{n2}, \Phi_{n1}^{n-2}\Phi_{n2}^2, \Phi_{n1}^{n-3}\Phi_{n2}^3, \ldots
$$

$$
\ldots \Phi_{n1}^3\Phi_{n2}^{n-3}, \Phi_{n1}^2\Phi_{n2}^{n-2}, \Phi_{n1}\Phi_{n2}^{n-1}, \Phi_{n2}^n
$$
Vanishing integral rule

The quantum mechanical integral

\[ I = \int \psi'' \hat{O} \psi'' \, d\tau \]

must vanish (i.e., be = 0) unless the integrand

\[ \psi'' \hat{O} \psi'' \]

contains a totally symmetric component in the symmetry group(s) of the Hamiltonian.
Totally symmetric component?

All groups have a totally symmetric irreducible representation $\Gamma^{(s)}$, e.g.

<table>
<thead>
<tr>
<th>$\mathcal{C}_{2v}(M)$</th>
<th>$E$</th>
<th>(12)</th>
<th>$E^*$</th>
<th>(12)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\mathcal{C}_{2v}$</td>
<td>$E$</td>
<td>$C_{2b}$</td>
<td>$\sigma_{ab}$</td>
<td>$\sigma_{bc}$</td>
</tr>
<tr>
<td>Equiv. rot.</td>
<td>$R^0$</td>
<td>$R_b^\pi$</td>
<td>$R_c^\pi$</td>
<td>$R_a^\pi$</td>
</tr>
</tbody>
</table>

| $A_1$ | 1 | 1 | 1 | 1 |
| $A_2$ | 1 | 1 | -1 | -1 |
| $B_1$ | 1 | -1 | -1 | 1 |
| $B_2$ | 1 | -1 | 1 | -1 |

In the totally symmetric representation, each group element is represented by the $1 \times 1$ matrix 1. The group $\{1\}$ is homomorphic to any group.

The representation of $\psi^{*}O\psi''$ must be

$$\Gamma = n^{(s)} \Gamma^{(s)} \oplus \ldots \text{ with } n^{(s)} \neq 0$$

in order that the integral can be non-vanishing.
Diagonalizing the molecular Hamiltonian

Schrödinger equation

\[ \hat{H} \psi_j = E_j \psi_j \]

\[ \psi_j = \sum_n c_{jn} \psi_n^0 \]

Eigenvalues and functions are found by diagonalization of a matrix with elements

\[ H_{mn} = \int (\psi_m^0)^* \hat{H} \psi_n^0 d\tau \]

We apply the vanishing integral rule
Diagonalizing the molecular Hamiltonian

\[ H_{mn} = \int (\psi_m^0)^* \hat{H} \psi_n^0 d\tau \]

The Hamiltonian is invariant under symmetry operations so the integrand in \( H_{mn} \) generates the product characters

\[ \chi^\Gamma[R] = \chi^{\Gamma_n}[R] \chi^{\Gamma_m}[R]^* \]

The number of times that the totally symmetric representation occurs is

\[ a^{\Gamma(s)} = \frac{1}{\hbar} \sum_R \chi^\Gamma[R] = \frac{1}{\hbar} \sum_R \chi^{\Gamma_n}[R] \chi^{\Gamma_m}[R]^* = \delta_{nm} \]
Diagonalizing the molecular Hamiltonian

\[ a^{\Gamma(s)} = \frac{1}{\hbar} \sum_{R} \chi^{\Gamma}[R] = \frac{1}{\hbar} \sum_{R} \chi^{\Gamma n}[R] \chi^{\Gamma m}[R]^* = \delta_{nm} \]

\( H_{mn} \) can only be non-vanishing if \( \psi^0_m \) and \( \psi^0_n \) belong to the same irreducible representation.

The Hamiltonian matrix factorizes, for example for \( \text{H}_2\text{O} \)

Computing time for diagonalization

\( \propto N^3 \) without factorization

\( \propto 4 \left( \frac{N}{4} \right)^3 = \propto \frac{N^3}{16} \) with factorization;
Intensities

For a gas phase sample illuminated by a weak electromagnetic radiation field the line strength of an electric dipole transition between all possible states $\Phi''_{rve}$ having energy $E''_{rve}$, and all possible states $\Phi'_{rve}$ having energy $E'_{rve}$, is

$$S(f \leftarrow i) = \sum_{\Phi'_{rve}, \Phi''_{rve}} \sum_{A=X,Y,Z} \left| \int \Phi'_{rve}^* \mu_A \Phi''_{rve} d\tau \right|^2,$$

where $d\tau = dX_2 dY_2 dZ_2 \ldots dX_l dY_l dZ_l$ is the volume element for integration over the internal coordinate space of the $l$ particles.

$\mu_A$ ($A = X, Y, Z$) is a space-fixed component of the molecular dipole moment

$$\mu_A = \sum_r C_r e A_r$$

$C_r e$ is the charge, $A_r$ the $A$ coordinate of particle $r$
Selection rules for transitions

So the intensity of a rotation-vibration transition is proportional to the square of

\[ I_{TM} = \int \Phi^*_{rve} \mu_A \Phi_{rve} \, d\tau \]

Vanishing integral rule: For the integral to be non-vanishing, the integrand must have a totally symmetric component.
Symmetry of $\mu_A$ for H$_2$O

Axis system $XYZ$ with origin in molecular center of mass; the protons are labeled 1, 2

Both protons have the charge $+1e$

\[
(12) (X_1, Y_1, Z_1) = (X_2, Y_2, Z_2) \\
(12) (X_2, Y_2, Z_2) = (X_1, Y_1, Z_1) \\
(12) (X_3, Y_3, Z_3) = (X_3, Y_3, Z_3)
\]

\[
\mu_A = \sum_r C_r eA_r
\]

\[
(12) \mu_A = \mu_A
\]
Symmetry of $\mu_A$ for H$_2$O

$$\mu_A = \sum_r C_r e A_r$$

$$E^* (X_1, Y_1, Z_1) = (-X_1, -Y_1, -Z_1)$$

$$E^* (X_2, Y_2, Z_2) = (-X_2, -Y_2, -Z_2)$$

$$E^* (X_3, Y_3, Z_3) = (-X_3, -Y_3, -Z_3)$$

$$E^* \mu_A = -\mu_A$$

$$(12)^* (X_1, Y_1, Z_1) = (-X_2, -Y_2, -Z_2)$$

$$(12)^* (X_2, Y_2, Z_2) = (-X_1, -Y_1, -Z_1)$$

$$(12)^* (X_3, Y_3, Z_3) = (-X_3, -Y_3, -Z_3)$$

$$(12)^* \mu_A = -\mu_A$$
Symmetry of $\mu_A$ for $\text{H}_2\text{O}$

\[(12) \mu_A = \mu_A \]

\[E^* \mu_A = -\mu_A \]

\[(12)^* \mu_A = -\mu_A \]

\[\Gamma^* = A_2 \]

<table>
<thead>
<tr>
<th>$C_{2v}$ (M):</th>
<th>$E$</th>
<th>$(12)$</th>
<th>$E^*$</th>
<th>$(12)^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$:</td>
<td>$E$</td>
<td>$C_{2b}$</td>
<td>$\sigma_{ab}$</td>
<td>$\sigma_{bc}$</td>
</tr>
<tr>
<td>Equiv. rot.:</td>
<td>$R^0$</td>
<td>$R_b^{\Pi}$</td>
<td>$R_c^{\Pi}$</td>
<td>$R_a^{\Pi}$</td>
</tr>
<tr>
<td>$A_1$:</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_2$:</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_1$:</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_2$:</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>
Symmetry of $\mu_A$ generally

$P \mu_A = \mu_A; \ P$ „pure“ permutation

$P^* \mu_A = -\mu_A; \ P^*$ permutation-inversion

$\Gamma^*$ has character +1 under all „pure“ permutations $P$,
$\quad -1$ under all permutation-inversions $P^*$

$\mu_A$ has symmetry $\Gamma^*$