Lecture #30: What is in a Character Table and How do we use it?

Last time
matrix representations of symmetry operators
representations of group — same multiplication table as symmetry operators
characters of matrix representations (all we need for most applications)
generate representation from convenient set of objects (basis vectors)

GOT
character table
irreducible representations generalization of odd/even
notation symmetry label for multi-dimensional integral with several non-commuting symmetry operators
GOAL
reduction of reducible representations

generate and reduce reducible representations

how do we get and use the fancy labels to the right of characters
(a, b, c)→(x, y, z) [conventions for x, y, z,
I_a ≤ I_b ≤ I_c for a, b, c]
selection rules: pure rotation and rotation-vibration and Raman.
nature of various types of vibration.

Example:

\[
\begin{array}{cccccc}
\text{E} & 2\text{C}_3(z) & 3\text{C}_2(\perp) & \sigma_h(xy) & 2\text{S}_3(z) & 3\sigma_v \\
A_1' & 1 & 1 & 1 & 1 & 1 & 1 \\
A_2' & 1 & 1 & -1 & 1 & 1 & -1 \\
E' & 2 & -1 & 0 & 2 & -1 & 0 \\
A_1'' & 1 & 1 & 1 & -1 & -1 & -1 \\
A_2'' & 1 & 1 & -1 & -1 & -1 & 1 \\
E'' & 2 & -1 & 0 & -2 & 1 & 0 \\
\end{array}
\]

(.rotational level symmetries and perturbations)
Rotations, Translations, IR selection rules,
p–orbitals
electronic selection rules
(magnetic dipole)
Polarizability, Raman Selection Rules,
d–orbitals

\[ x^2 + y^2, z^2 \]
\[ (x, y) \]
\[ (x^2 - y^2, xy) \]
\[ (R_x, R_y) \]
\[ (xy, yz) \]

order of group \( g = 12 = \sum n_\nu^2 \) (n\( _\nu \) is order of \( \nu \)-th irreducible representation) equal to number of classes: 1 + 2 + 3 + 1 + 2 + 3

R\( _z \) “belongs to” \( A_2' , \) \( z \) (or \( T_z \) belongs to \( A_2'' \)
Use picture to generate representation

Use picture to generate representation

\[
\begin{pmatrix}
E & C_3 & C_2 & \sigma_h & S_3 & \sigma_v \\
R_z & 1 & 1 & -1 & 1 & +1 & -1 & A' \\
T_z & 1 & 1 & -1 & -1 & -1 & 1 & A'' \\
\end{pmatrix}
\]

show with cartoons why \( R_z \leftrightarrow A'_2 \) from these characters

\((x,y)\) means symmetry operation transforms \( x \) into \( y \) (must generate 2D representation using \( x \) and \( y \))

**Selection rules:** integrand must contain totally symmetric representation.

\[
\int \psi_i \hat{O} \psi_f \, d\tau \neq 0
\]

Direct Product: \( \Gamma (\psi_i) \otimes \Gamma (\hat{O} \psi_f) \) must include \( \Gamma (\psi_f) \) because direct product of any irreducible representation with itself contains the totally symmetric representation.

\[
\chi_i \otimes \chi_f \equiv \left( \chi^i \left( R_1 \right) \chi^j \left( R_1 \right), \chi^i \left( R_2 \right) \chi^j \left( R_2 \right), \ldots \right)
\]

Example: \( E' \otimes E'' = (4 \ 0 \ -4 \ -1 \ 0) \)

(shortcuts)

\[
\begin{align*}
A \otimes B &= B \\
g \otimes u &= u \\
1 \otimes 2 &= 2
\end{align*}
\]

Decomposition of \( (4 \ 1 \ 0 \ -4 \ -1 \ 0) \):

\[
\begin{align*}
a_{A'_2} &= \frac{1}{12} \left[ 4 \cdot 1 \cdot 1 + 1 \cdot 2 \cdot 1 + 0 - 4 \cdot 1 \cdot 1 - 1 \cdot 2 \cdot 1 + 0 \right] = 0 \\
a_{E'} &= \frac{1}{12} \left[ 4 \cdot 2 \cdot 1 + 1 \cdot 2 (-1) + 0 - 4 \cdot 1 \cdot (-2) - 1 \cdot 2 \cdot 1 + 0 \right] = 1 \\
a_{A''} &= 1 \\
a_{A''} &= 1
\end{align*}
\]

So now we know how to work out all selection rules.

Best to work specific example of \( D_{3h} \) molecule \( \text{BCl}_3 \).
Generate 3N dimensional representation. 

\[ \chi^{\text{red}}_{\text{E}} = \begin{pmatrix} 12 & 1 + 2 \cos \frac{2\pi}{3} & 2(1-2) & 4(2-1) & -1+2 \cos \frac{2\pi}{3} & 2(2-1) \end{pmatrix} \]

\[ \chi^{\text{red}} = \chi^{A_1'} + 3\chi^{E'} + 2\chi^{A_2''} + \chi^{A_1''} + \chi^{E''} \] (total of 12 degrees of freedom)

3 translations \( E' \leftrightarrow (x,y) \)
\[ A_2'' \leftrightarrow z \]

3 rotations \( A_2' \leftrightarrow R_z \)
\[ E'' \leftrightarrow (R_x, R_y) \]

This leaves 6 vibrations

\[ \chi^{\text{vib}} = \chi^{A_1'} + 2\chi^{E'} + \chi^{A_2''} \] (total of 6)

(four normal modes, two are doubly degenerate)

We can go further - to figure out bend vs. stretch or mixed character of the 4 normal modes (especially when there is only 1 mode in a symmetry class)

Thus \( A_1' \) pure symmetric stretch
\( A_2'' \) pure bend (out of plane – because \( \chi(\sigma_h) = -1 \))
\( 2E' \) mixed bend and stretch

scissors
\[ \text{pseudo rotation} \]

one out, two in
also pseudo rotation
Now we are ready to work out selection rules for vibration-rotation spectra

$$\Gamma^{(v_1, v_2, v_3, v_4)} = \chi_1^{v_1} \otimes \chi_2^{v_2} \otimes \chi_3^{v_3} \otimes \chi_4^{v_4}$$

$$\Gamma^{(0,0,0,0)} = A_1'$$

<table>
<thead>
<tr>
<th>fundamentals</th>
<th>overtones</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma^{(1 0 0 0)}$</td>
<td>$A_1'$</td>
</tr>
<tr>
<td>$\Gamma^{(0 1 0 0)}$</td>
<td>$A_2''$</td>
</tr>
<tr>
<td>$\Gamma^{(0 0 1 0)}$</td>
<td>$E'$</td>
</tr>
<tr>
<td>$\Gamma^{(0 0 0 1)}$</td>
<td>$E'$</td>
</tr>
</tbody>
</table>

$$E' \otimes E' = (4 1 0 4 1 0) = (A_1' + A_2'' + E')$$

Selection rules for fundamental bands

- $\Gamma' \otimes \Gamma''$
  - (1 0 0 0) $\leftarrow$ (0 0 0 0) $A_1'$
  - (0 1 0 0) $A_2''$
  - (0 0 1 0) $E'$
  - (0 0 0 1) $E'$

in order for transition integral to be nonzero, need $\Gamma_{x, y, or z} = \Gamma' \otimes \Gamma''$

<table>
<thead>
<tr>
<th>mode</th>
<th>$A_1'$</th>
<th>$A_2''$</th>
<th>$E'$</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>IR forbidden</td>
<td>IR allowed</td>
<td>IR allowed</td>
</tr>
<tr>
<td>#2</td>
<td>$z$</td>
<td>$x, y$</td>
<td></td>
</tr>
</tbody>
</table>

But how will the rotational transitions behave?
Recall $\mathbf{M}_j(Q) = \hat{a} \left[ M_{j,a}(0) + \sum_i \left( \frac{\partial M_{j,a}}{\partial Q_i} \right)_e Q_i + \ldots \right]$

$+ \hat{b} \left[ M_{j,b}(0) + \sum_i \left( \frac{\partial M_{j,b}}{\partial Q_i} \right)_e Q_i + \ldots \right]$

$+ \hat{c} \left[ M_{j,c}(0) + \sum_i \left( \frac{\partial M_{j,c}}{\partial Q_i} \right)_e Q_i + \ldots \right]$

So mode #1 $A'_{1}$

$\frac{\partial M_{j,abc}}{\partial Q_1} = 0$

#2 $A''_{2}$

$\frac{\partial M_{j,x}}{\partial Q_2} \neq 0$

#3 $\Gamma'_{3}$

$\frac{\partial M_{j,x \text{ or } y}}{\partial Q_{3 \text{ or } 4}} \neq 0$

For $\text{BCl}_3$ an oblate symmetric top

- Mode #2 fundamental is c type (||)
- Mode #3,4 fundamentals are a,b type (⊥)
<table>
<thead>
<tr>
<th></th>
<th>$\Delta K = 0$</th>
<th>weak $Q$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta K = \pm 1$</td>
<td>strong $Q$</td>
</tr>
</tbody>
</table>

General procedure
3N dimensional $\chi^\text{RED}$
find (and classify) all normal mode symmetries
$(x,y,z) \leftrightarrow (a,b,c)$
$\uparrow$ highest order $C_n$
avtivity and rotational type of each vibrational fundamental
Raman

Figures from Bernath:

Image removed due to copyright restrictions.
The E-A₁ energy level diagram is given in Figure 7.51. The energy level structure of an E vibrational state is complicated by the presence of a first order Coriolis interaction between the two components. The selection rules are $\Delta K = \pm 1$ and $\Delta J = 0, \pm 1$. Note also that for $\Delta K = +1$ the transitions connect to the $(+\ell)$ stack while for $\Delta K = -1$ they connect with the $(-\ell)$ stack. The transition can again be represented by a superposition of sub-bands. Notice how the sub-bands do not line up as they do for a parallel transition, but they spread out (Figure 7.52). Each sub-band is separated by approximately $2\{A(1-\zeta)-B\}$. This gives rise to a characteristic pattern of nearly equally spaced Q branches (Figure 7.53).
What if BCl$_3$ were not D$_{3h}$ (planar)?

C$_{3v}$ (like NH$_3$) prolate or oblate, depending on apex angle

C$_{2v}$ planar (near oblate) tee
Fall, 2008

planar (near prolate)  \[ \text{wye} \]

\[ z \]
\[ \uparrow a \]
\[ \text{planar (3 different bond lengths or 3 different angles)} \]

Truth table

<table>
<thead>
<tr>
<th>point group</th>
<th># of normal modes</th>
<th>pure rotational spectrum type</th>
<th># of IR active fundamentals</th>
<th>Rotational type of IR fundamentals</th>
<th>Raman active fundamentals</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{3h} )</td>
<td>4</td>
<td>—</td>
<td>3</td>
<td>1-c, 2-a,b</td>
<td></td>
</tr>
<tr>
<td>( C_{3v} )</td>
<td>4</td>
<td>c-oblate ( \text{a-prolate} )</td>
<td>4</td>
<td>2-c, 2-a,b</td>
<td></td>
</tr>
<tr>
<td>( C_{2v} )</td>
<td>6</td>
<td>asymmetric hybrid a,b or b,c</td>
<td>6</td>
<td>3-a, 2-b, 1-c</td>
<td></td>
</tr>
</tbody>
</table>

For \( D_{3h} \) here will be two \( \perp \) polarized (\( E' \)) fundamentals

There will be one \( \parallel \) polarized (\( A''_{2} \)) fundamental

There will be one forbidden (i.e. not observable by IR) fundamental (\( A'_{1} \))

(a,b)-type \( \perp \) polarized (i.e. \( \Delta K = \pm 1 \)) \text{oblate top} vibrational spectrum (the two \( E' \) modes in \( \text{BCl}_3 \))

\[ E_{JK}^{\text{ROT}} = BJ(J + 1) + (C - B)K^2 \]

\( C - B < 0 \)

Strong Q branches. Q branch “spikes” dominate band profile.

\[ K' - K' \]

\[ RQ_0(J) = (C - B)[1^2 - 0^2] \]

\( \text{since } \Delta B \text{ is small} \)

\[ RQ_1(J) = (C - B)[2^2 - 1^2] \]

\[ P'Q_1(J) = (C - B)[0^2 - 1^2] \]

etc.
(c)-type \parallel polarized (i.e. \Delta K = 0) oblate top vibrational spectrum. (the one \( A'' \) out-of plane bend from BCl\(_3\))

weak Q branches, except at \( J \approx K \) and high \( K \)
\( \Delta K = 0 \) only. All \( ^3Q_x(J) \) tend to pile up as spike at band origin.

(b,c)-type \perp prolate top bands (x,y,z)\leftrightarrow(b,c,a)
Strong Q branches
- \( ^8Q_0 (A - B) \) 1
- \( ^8Q_1 (A - B) \) 3

Looks very similar to \perp type oblate band except that branches are labeled in reverse order and more spread out (less overlap of K sub-bands) because usually \( |A - B|_{prolate} \gg |B - C|_{oblate} \)

a-type (||) prolate \( \Delta K = 0 \), weak Q except at low \( J \approx K \)

Asymmetric tops: Resemble symmetric top when \( J \approx K \)
More complicated because \( E_{J_k,K_x} \) can’t be separated into J-dependent and K-dependent additive terms.
Special simplification for linear molecules.
zero-point level has only $\ell = 0$ vibrational angular momentum.
There is no $K$ projection of $J$.
Bending mode is $\pi \leftrightarrow \ell = 1$.
$\| \text{ type } \Delta \ell = 0$ (anti-symmetric stretch),
$\perp \text{ type } \Delta \ell = \pm 1$ (bend)

<table>
<thead>
<tr>
<th>Benzene</th>
<th>thru atoms</th>
<th>thru bonds</th>
<th>h = 24</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>2C₁</td>
<td>2C₃</td>
<td>C₂</td>
</tr>
<tr>
<td>36</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[ \begin{align*}
D_{oh} & \quad D_6 \\
A_1' & = \frac{1}{24} (-12 + 12 + 12 + 36) = 2 \\
A_{2g} & = \frac{1}{24} (36 + 12 + 12 - 12) = 2 \\
B_{1g} & = \frac{1}{24} (36 - 12 - 12 - 12) = 0 \\
B_{2g} & = \frac{1}{24} (36 + 12 - 12 + 12) = 2 \\
E_{1g} & = \frac{1}{24} [72 - 24] = 2 \\
E_{2g} & = \frac{1}{24} [72 + 24] = 4 \\
E_{2u} & = \frac{1}{24} [72 + -24] = 2 \\
A_{1u} & = \frac{1}{24} (36 - 12 - 12 - 12) = 0 \\
A_{2u} & = \frac{1}{24} (36 + 12 - 12 + 12) = 2 \\
\end{align*} \]
### symmetries and numbers of normal modes

<table>
<thead>
<tr>
<th></th>
<th>2A₁</th>
<th>2g − 1</th>
<th>0u</th>
</tr>
</thead>
<tbody>
<tr>
<td>4A₂</td>
<td>2g</td>
<td>2u − 1</td>
<td></td>
</tr>
<tr>
<td>2B₁</td>
<td>0g</td>
<td>2u</td>
<td></td>
</tr>
<tr>
<td>4B₂</td>
<td>2g</td>
<td>2u</td>
<td></td>
</tr>
<tr>
<td>6E₁</td>
<td>2g − 1</td>
<td>4u − 1</td>
<td></td>
</tr>
<tr>
<td>6E₂</td>
<td>4g</td>
<td>2u</td>
<td></td>
</tr>
</tbody>
</table>

### translation:
- $A_{2u}(z)$, $E_{1u}(x,y)$

### rotation:
- $A_{2g}(R_z)$, $E_{1g}(R_x, R_y)$