Carbonyl stretch

Four vectors as Basis

\[ \Gamma_{CO,\text{stretch}} = A_{1g} + B_{1g} + E_u \]

IR: \( E_u \)  
Raman: \( A_{1g} + B_{1g} \)

Two degenerate mode  
One absorption peak

\[
\begin{array}{ccccccccccc}
\Gamma & 4 & 0 & 0 & 2 & 0 & 0 & 0 & 4 & 2 & 0 \\
\hline
D_{4h} & E & 2C_4 & C_2 & 2C_2 & 2C_2' & i & 2S_4 & \sigma_h & 2\sigma_v & 2\sigma_d \\
\end{array}
\]
Exclusion rule:

*In centrosymmetric molecules, no IR-active vibration can also be Raman active and vice versa.*

Point group containing the inversion operation \( i \) have two sets of irreducible representation, \( g \) and \( u \).

Set \( u \): \( \rightarrow x, y, z \)

Set \( g \): \( \rightarrow xy, xz, yz, z^2, x^2-y^2 \)

<table>
<thead>
<tr>
<th></th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( i )</th>
<th>( \sigma_h )</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_x )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( R_z )</td>
<td>( x^2, y^2, z^2, xy )</td>
</tr>
<tr>
<td>( B_x )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>( R_x, R_y )</td>
<td>( xz, yz )</td>
</tr>
<tr>
<td>( A_u )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>( z )</td>
<td></td>
</tr>
<tr>
<td>( B_u )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( x, y )</td>
<td></td>
</tr>
</tbody>
</table>

The \( \text{C-Cl} \) stretching modes of \( \text{CCl}_4 \) have \( A_1 + T_2 \) symmetry:

<table>
<thead>
<tr>
<th>( \Gamma )</th>
<th>4</th>
<th>1</th>
<th>0</th>
<th>0</th>
<th>2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_d )</td>
<td>E</td>
<td>8( C_3 )</td>
<td>3( C_2 )</td>
<td>6( S_4 )</td>
<td>6( \sigma_d )</td>
</tr>
<tr>
<td>( A_1 )</td>
<td>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>
<td>-1</td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( T_1 )</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>( T_2 )</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>
Optical activity:

An optical active molecule is one that rotates the plane of the polarized light.

A molecule is optically active only if it cannot be superimposed on its mirror image (chiral or dissymmetric):

1. if it does not contain an $S_n$ axis;
2. if it belongs to a point group $C_1$, $C_n$ or $D_n$.

6.1.1 Superimposable and Nonsuperimposable
Superimposable image and mirror image of hammer

Carvone

Chem 104A, UC, Berkeley
Examples with $C_1$ symmetry: no symmetry elements except the onefold rotation metry is asymmetry.
Symmetry & Group Theory

✔ Predict vibrational spectra
✔ Determine optical activity

Construct bonding based on atomic orbitals

Access reaction pathway