Lecture 8

Symmetry II: Vibrational Spectroscopy

Reading: Shriver and Atkins 6.4-6.5, 8.4
Recall from last class...

Character tables identify the properties of a molecule

- columns correspond to classes of group elements (i.e., symmetry operations).
- rows correspond to irreducible group representations: they describe the allowed transformations of an object in the group.
- The entries consist of characters, related to the trace of the matrices representing the group elements.

\[ \begin{array}{c}
\text{p}_x \\
\begin{array}{c}
\text{d}_x \\
\end{array}
\end{array} \]
Vibrational Spectroscopy

- Used to characterize a molecule’s strength, stiffness, and number of bonds.
- Also used to detect presence of known compounds, monitor changes in concentration of a species during a reaction, determine components of an unknown compound, and determine the likely structure.

- A molecular vibration occurs when atoms in a molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion.

- Typical frequencies: \( <10^{12}-10^{14} \) Hz

\[
E_n = (n + \frac{1}{2})\hbar \omega \quad \omega = \sqrt{\frac{k}{\mu}}
\]
Normal Modes

• Different, independent vibrations of a molecule

• A molecule consisting of $N$ atoms has $3N-6$ normal modes if it is non-linear and $3N-5$ normal modes if it is linear

• Example: $\text{CO}_2 \rightarrow 4$ normal modes
  • Only normal modes corresponding to a changing electric dipole moment can absorb radiation
Infrared Spectroscopy

- An IR vibrational spectrum is obtained by exposing the sample to IR radiation and recording the variation of the absorbance with frequency.
- Wavelengths of ~2000-16000nm (~2x10^{13}-1.2x10^{14} Hz)
- Glass and water cannot be used, unless the spectral bands of interest occur at frequencies not absorbed by either (typically use CsI optical windows)
- Depends on a molecule’s electric dipole moment

![Infrared Spectroscopy Diagram](image)
General Trends in Infrared Spectroscopy

1. Stretching frequencies are higher than corresponding bending frequencies. (It is easier to bend a bond than to stretch or compress it.)

2. Bonds to H have higher stretching frequencies than those to heavier atoms.

3. Triple bonds have higher stretching frequencies than corresponding double bonds, which in turn have higher frequencies than single bonds (Except for bonds to hydrogen).

[Diagram showing wavelength (microns) vs. frequency (cm⁻¹) with stretching and bending vibrations indicated.]
Raman Spectroscopy

- In Raman spectroscopy, the sample is exposed to visible light.
- Most photons are elastically scattered (with no change of frequency).
- Some are inelastically scattered, with frequency differences from the incident radiation equivalent to the vibrational frequencies of the molecule.
- Aqueous solutions can be used, but linewidths are usually larger than with IR.
  - depends on a molecule’s polarizability
IR versus Raman

- IR: depends on electric dipole moment of molecule: \( p = qd \) (\( d = z, y, z \))
- Raman: depends on polarizability: \( \alpha = p/E \) ([E]=V/m, [p]=Cm, [\alpha]=Cm^2/V)
IR versus Raman

- IR: The symmetry of the vibration must be the same as that of x, y, z in the character table
- Raman: the symmetry must be a quadratic function (i.e, xy or $x^2$)

In cases where it is difficult to judge the change in polarizability of a normal mode, can use the exclusion rule:

*If a molecule has a center of inversion, none of its modes can be both IR and Raman active*
Example: $\text{CO}_2$

Which modes are IR or Raman Active?

- Symmetric stretch
- Antisymmetric stretch
- Bend
Example: $\text{CO}_2$

Which modes are IR or Raman Active?

- **Symmetric stretch**: IR inactive
- **Antisymmetric stretch**: IR active
- **Bend**: IR active
Example: $\text{CO}_2$

Which modes are IR or Raman Active?

- **Symmetric stretch**
  - IR inactive
  - Could be Raman active (*it is*)

- **Antisymmetric stretch**
  - IR active
  - Cannot be Raman active

- **Bend**
  - IR active
  - Cannot be Raman active

- **Bend**
  - IR active
  - Cannot be Raman active
Raman activity from symmetries of normal modes

Consider a square planar Pd complex

Cis ($C_{2v}$ symmetry) $E, C_2, \sigma_v, \sigma_v'$

```
Cl
Pd
H_3N
NH_3
```

Trans ($D_{2h}$ symmetry) $E, 2C_3, 3C_2, \sigma_h, 3\sigma_v', 2S_3$

```
Cl
Pd
NH_3
Cl
```

- IR $\rightarrow$ $x, y, z$ in the character table
- Raman $\rightarrow$ quadratic function
Cis isomer:

Cis (C$_{2v}$ symmetry)

E, C$_2$, $\sigma_v$, $\sigma'_v$

Cl

H$_3$N ——— Pd ——— Cl

NH$_3$

<table>
<thead>
<tr>
<th>$C_{2v}$</th>
<th>E</th>
<th>C$_2$</th>
<th>$\sigma_v$</th>
<th>$\sigma'_v$</th>
<th>h=4</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>z</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1'</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x$, $R_y$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$, $R_x$</td>
</tr>
</tbody>
</table>

Both are IR active ($A_1 \rightarrow z$, $B_2 \rightarrow y$). Also, both are Raman active.
Trans isomer:

Trans ($D_{2h}$ symmetry) E, 2$C_3$, 3$C_2$, $\sigma_h$, 3$\sigma_v'$, 2$S_3$

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_2 (z)$</th>
<th>$C_2 (y)$</th>
<th>$C_2 (x)$</th>
<th>i</th>
<th>$\sigma (xy)$</th>
<th>$\sigma (xz)$</th>
<th>$\sigma (yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{3g}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$A_u$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>x</td>
</tr>
</tbody>
</table>

$g$ (gerade): symmetric to inversion
$u$ (ungerade): antisymmetric to inversion

$\text{Cl}$  
$\text{H}_3\text{N} \rightarrow \text{Pd} \rightarrow \text{NH}_3$  
$\text{Cl}$
Trans isomer:

Trans (D$_{2h}$ symmetry) E, 2C$_3$, 3C$_2$, $\sigma_h$, 3$\sigma'$, 2S$_3$

Raman active ($A_g \rightarrow x^2$)  
IR active ($B_{2u} \rightarrow y$)

<table>
<thead>
<tr>
<th>D$_{2h}$</th>
<th>E</th>
<th>C$_2$ (z)</th>
<th>C$_2$ (y)</th>
<th>C$_2$ (x)</th>
<th>i</th>
<th>$\sigma$ (xy)</th>
<th>$\sigma$ (xz)</th>
<th>$\sigma$ (yz)</th>
<th>$x^2$, $y^2$, $z^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_g$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B$_{2u}$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>y</td>
</tr>
</tbody>
</table>
Spectra for these Pd complexes

- In Pd-Cl stretching region, the cis isomer has two bands in both IR and Raman spectra (since both modes are IR and Raman active).

- The trans isomer has only one band at a different frequency in each spectra (since only the symmetric mode IR active, and only the antisymmetric mode is Raman active).
Ni(CO)$_4$ is characterized by four CO displacements. How many IR and Raman bands are expected?

All 4 displacements away from Ni

2 in, 2 out
Tetrahedral Ni(CO)$_4$

![Diagram of Ni(CO)$_4$]

<table>
<thead>
<tr>
<th>$T_d$</th>
<th>E</th>
<th>$8C_3$</th>
<th>$3C_2$</th>
<th>$6S_4$</th>
<th>$6\sigma_d$</th>
<th>$h=24$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

- All four displacement vectors remain unchanged
- Only one remains the same
- Two remain the same
- None remain the same
**Tetrahedral Ni(CO)₄**

<table>
<thead>
<tr>
<th>Tₐ</th>
<th>E</th>
<th>8C₃</th>
<th>3C₂</th>
<th>6S₄</th>
<th>6σₐ</th>
<th>h = 24</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>A₂</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>Raman active</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>-1</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>(2x² - y² - z², x² - y²)</td>
</tr>
<tr>
<td>T₁</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>(Rₓ, Rᵧ, Rₚ) IR &amp; Raman active</td>
</tr>
<tr>
<td>T₂</td>
<td>3</td>
<td>0</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>(x, y, z) (xy, yz, zx)</td>
</tr>
</tbody>
</table>

This set of characters corresponds to the sum of characters of A₁ and T₂

<table>
<thead>
<tr>
<th>Tₐ</th>
<th>E</th>
<th>8C₃</th>
<th>8C₂</th>
<th>6S₄</th>
<th>6σₐ</th>
<th>h=24</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

- All four displacement vectors remain unchanged
- Only one remains the same
- Two remain the same
- None remain the same

Therefore, one IR band and two Raman bands in CO stretching region