Vibrational Spectroscopy

Big Idea and the Boltzmann distribution. Energy levels and selection rules determine spectra.

Skills

- Determine bond spring constants from IR $\tilde{\nu}$ values

- Apply the gross selection rules for IR

- Apply the specific selection rule for IR
Energy Levels: model as harmonic oscillator

\[ E_n = h \nu (n + \frac{1}{2}) \quad \nu = \frac{1}{2\pi} \sqrt{\frac{E}{\mu}} \]

\[ \begin{array}{c}
E \\
| \downarrow \\
n=1 \\
| \downarrow \\
n=2 \\
| \downarrow \\
n=3 \\
| \downarrow \\
n=4 \\
\end{array} \]

(for large \( n \), use energy levels from Morse potential instead)

But which transitions are possible? Which molecules absorb?
Vibrational Modes

- 3 modes (x, y, z) per atom
- 3N total for N-atom molecule
- 3 translational modes
- 3 rotational modes (non-linear)
or
- 2 rotational modes (linear)

\[ 3N - 6 \text{ (non-linear)} \]
\[ 3N - 5 \text{ (linear)} \]
Normal Modes

H₂O: 3 atoms, non-linear, so
3N - 6 = 9 - 6 = 3 vibrational modes

\[ \text{H} \rightleftharpoons \text{O} \rightleftharpoons \text{H} \] symmetric stretch

\[ \text{H} \rightarrow \text{O} \rightarrow \text{H} \] asymmetric stretch

\[ \text{H} \rightarrow \text{O} \rightarrow \text{H} \] bending

If adjacent bonds have very different k values, vibrations are largely uncoupled.

Which vibrational modes are IR-active?
The vibrational absorption (IR) gross selection rule.

Consider $\text{CO}_2 = \overset{\text{O}}{\text{C}} = \overset{\text{O}}{\text{C}}$

Which vib modes are IR-active?

Asymmetric stretch can be excited by IR

Bond can be excited by IR

Can symmetric stretch? NO

Gross Selection Rule: mode is IR active if dipole moment changes during vibration.