**Assumed knowledge**

There are $3N-6$ vibrations in a non-linear molecule and $3N-5$ vibrations in a linear molecule. Only modes that lead to a change in the dipole moment are IR active. For each mode, bands with $\Delta \nu = \pm 1, 2, 3$ are possible but the overtones ($\Delta \nu > 1$) are increasingly weak. Combination bands where more than one mode is simultaneously excited are also possible.

**Learning outcomes**

- Be able to pick the vibrational modes in a molecule which are likely to be coupled and those which are likely to be local modes
- Be able to explain the appearance of IR spectra of terms of (strong) fundamental transitions and weaker overtones and combinations
- Be able to use Jablonski diagrams to assign spectra

**Local Modes**

- Although all vibrations in a molecule can couple, for a number of normal modes the bulk of the vibrational amplitude can be found on a small number of atoms.
- This frequently occurs when the natural frequency of an individual vibration does not closely match that of other vibrations in the molecule.

- **CH$_4$**
  - $2900 \text{ cm}^{-1}$
  - $3100 \text{ cm}^{-1}$

- **CH$_3$Cl**
  - $3100 \text{ cm}^{-1}$
  - $3000 \text{ cm}^{-1}$
  - $700 \text{ cm}^{-1}$
  - $3100 \text{ cm}^{-1}$ (×2)

- All C-H equivalent: all C-H stretches are completely mixed
- All C-H equivalent: all C-H stretches are completely mixed
- C-Cl frequency is much lower: almost completely uncoupled

**How can you pick local modes?**

**2 main things to look for:**

1. Vibration involves atom(s) with only one bond: this means the atom vibrates into space, rather than against other atoms.
2. The vibrating atom(s) have a different natural vibrational frequency to the connected groups (atoms and bonds): this means their vibration is OUT OF RESONANCE with their neighbors.
Which vibrations will be local modes?

Acetone: C-O and C-C stretches

IR Spectrum of Acetone

Which vibrations will be local modes?

- What type of vibrations will be local modes (with characteristic frequencies)?
**Jablonski diagrams**

At least for simple molecules, a full analysis of the vibrational spectrum is often possible:

- Work out the number \((3N-6)\) and IR activity of the vibrations
- The strongest bands are the *fundamentals*: single excitations of these modes \((\Delta \nu = 1)\)
- First, second, third... overtones: \(\Delta \nu = 2, 3, 4\...\) with rapidly decreasing intensity
- Combinations: simultaneous excitation of different vibrations: \(\Delta \nu = 1, 2, 3, 4\) for each mode with rapidly decreasing intensity
Normal Modes of H$_2$O

Polyatomic molecules can vibrate in many different ways
• H$_2$O contains 3 atoms so has $3N - 6 = 3$ vibrations
• Each is IR active

Vibrational Spectrum of H$_2$O

Polyatomic molecules can vibrate in many different ways
• $\nu_1 = 3657$ cm$^{-1}$, $\nu_2 = 1595$ cm$^{-1}$, $\nu_3 = 3756$ cm$^{-1}$
• Label excitations as ($\nu_1$, $\nu_2$, $\nu_3$)
• As first approximation, neglect effect of anharmonicity on energies

Vibrational Spectrum of OCS

Polyatomic molecules can vibrate in many different ways
• Linear so $3N-5 = 4$ vibrations
• Unlike CO$_2$, the C=O and C=S natural frequencies are different leading to incomplete mixing:

Vibrational Spectrum of OCS
Next lecture

- Raman spectroscopy

Week 12 tutorial and homework

- Spectroscopy worksheet in the tutorials
- Complete the practice questions from the lectures

Practice Questions

1. Assign the spectrum of OCS in as much detail as you can.
2. Two infrared spectra of hexane (C₆H₁₄) are shown overleaf. The top spectrum is a conventional mid-IR spectrum with assignment of the two main transitions indicated. The bottom spectrum extends form the mid-IR to the visible and shows a number of CH-stretch overtone transitions with ever decreasing intensity (note the scale factor for the intensity).
   a) Propose an assignment for the unidentified peak at about 4400 cm⁻¹ in the bottom spectrum
   b) The wavenumber of the fundamental CH-stretch transition from the top spectrum is ν = 2962 cm⁻¹. The wavenumber of the fourth CH-stretch overtone (i.e. the ν = 0→5 transition marked “5*”), from the bottom spectrum, is ν = 13401 cm⁻¹. Calculate the harmonic constant, ωₑ, and the anharmonicity constant, ωₑₓₑ, for the CH bond.
   c) Estimate the bond dissociation energy, D₀, of the CH bond in hexane.
   d) The tabulated CH bond energy is 411 kJ mol⁻¹. Comment on the agreement or disagreement with your answer to (c)