**Vibrations of Polyatomic Molecules**

- A diatomic has obviously only one type of vibration. How many different ways can a larger molecule vibrate?

- Consider a collection of $N$ atoms. With no bonding between them, each atom has 3 degrees of freedom corresponding to movement in the $x$, $y$, and $z$ directions.

**Assumed knowledge**

Only vibrations that give rise to a change in the dipole moment are IR active. A harmonic oscillator gives rise to a single peak in the IR spectrum as $\Delta \nu = \pm 1$. For a real molecule, bands with $\Delta \nu = 1, 2, 3$ are also possible but become increasingly weak.

**Learning outcomes**

- Be able to calculate the number of vibrations in a polyatomic molecule ($3N - 6$ or $3N-5$ if it is linear)
- Be able to describe vibrations as stretches or bends and recognize that the number of stretches is equal to the number of bonds.
- Be able to explain that all atoms oscillate at the same frequency in a normal mode
- Be able to explain why many normal modes give rise to characteristic frequencies
- Be able to explain the appearance of IR spectra of terms of (strong) fundamental transitions and weaker overtones and combinations

**Vibrations of Polyatomic Molecules**

- Now join the atoms by bonds:
  1. A general non-linear molecule
     a) move along $x$, $y$ or $z$
     b) rotate around $x$, $y$ or $z$

\[
\begin{align*}
3 \times \text{translations (along } x, y, z) &+ \\
3 \times \text{rotations (about } x, y, z) &+ \\
3N-6 \text{ vibrations} &\
\end{align*}
\]

3N degrees of freedom
Normal Modes of $H_2O$

Polyatomic molecules can vibrate in many different ways
- $H_2O$ contains 3 atoms so has $3N - 6 (3 \times 3 - 6) = 3$ vibrations

![Symmetric stretch](image1)  ![Asymmetric stretch](image2)  ![Bend](image3)

- Each normal mode has its own potential energy and force constant so its own set of energy levels

Normal Modes of $CO_2$

Polyatomic molecules can vibrate in many different ways
- $CO_2$ contains 3 atoms and is linear so has $(3 \times 3 - 5) = 4$ vibrations

![Symmetric stretch](image4)  ![Degenerate bends](image5)  ![Asymmetric stretch](image6)

Vibrations of Polyatomic Molecules

- Now join the atoms by bonds:
  1. A general linear molecule
     a) move along $x$, $y$ or $z$
     b) rotate around $y$ or $z$
     rotation about $x$ does not correspond to a genuine motion of the molecule

$3 \times $ translations (along $x$, $y$, $z$) + $2 \times $ rotations (about $x$, $y$, $z$) + $3N$-5 vibrations

3N degrees of freedom

Absorbing IR Light

To absorb light, the vibration must produce an oscillating charge
- it is not necessary for the molecule to have a dipole moment but one must be produced during the vibration

- $H_2O$: the symmetric and asymmetric stretches and the bend lead to a change in the dipole
- $CO_2$: only the asymmetric stretch and the bend leads to a change in the dipole

![Dipole](image7)  ![No dipole](image8)
**Exercise.....**

How many vibrational modes do these molecules have?

- **Ethylene, C₂H₄**
- **Ethanol, C₂H₅OH**
- **SF₆**

Which molecules can absorb radiation by vibrating?

**Normal Modes**

- The 3N-6 characteristic vibrations of a (non-linear) polyatomic molecule are all called “normal modes” of vibration.
- Some criteria for a vibration to be a suitable normal mode of vibration include:
  - The centre of mass cannot move (3 x translations)
  - There can be no overall rotation about the centre of mass (3 x rotations)
  - All atoms oscillate with the same frequency (though the amplitude of oscillation can be very small for some atoms in the molecule)

**Normal Modes**

- The individual stretches and bends of different bonds in a molecule are coupled together.
- They combine in analogous ways to orbitals.

- O 2s orbitals are perfectly matched in energy: mixing is complete.
- C-O bond stretches are perfectly matched in energy: mixing is complete.

- In phase combination:
  - Perfectly matched for 0 = C = O
  - Symmetric stretch for O = C = O

- Out of phase combination:
  - Asymmetric stretch for O = C = O
Normal Modes

- Stretches are analogous to σ bonds: they can be worked out using the atomic orbitals on the central atom which are used for σ bonding.

  C 2s and 2p, are used to σ bond:

  \( \sigma \) bonding C 2s and 2p, are used to σ bond:

  Take ‘black’ lobe as analogous to outward motion and ‘white’ lobe as analogous to inward motion.

  \[ \text{symmetric stretch} \]

  \[ \text{asymmetric stretch} \]

Normal Modes

- Stretches are analogous to σ bonds: they can be worked out using the atomic orbitals on the central atom which are used for σ bonding.

  - In methane, C uses its 2s and each of its three 2p orbitals to make σ bonds ("sp\(^3\))

  \[ \text{three degenerate asymmetric stretches} \]

Normal Modes

- In SF\(_6\), S uses its: 3s, each of its three 3p orbitals and 3d\(_{x^2-y^2}\) and 3d\(_{z^2}\)
Polyatomic IR Spectroscopy

- The extension from diatomic to polyatomic spectroscopy is straightforward...
- For a molecule with \( x \) vibrational modes:
  - \( x \) fundamental transitions: \( \Delta v_a = 1 \)
  - \( x \) first overtones, \( x \) second overtones etc: \( \Delta v_a = 2, \Delta v_a = 3, \ldots \)
  - \( v = 0 \) is still the dominant populated state at normal temperature

PLUS
- Combinations of vibrations are now possible where several vibrations are simultaneous excited
  - e.g. \( v = 0 \rightarrow (v_{\text{bend}} = 1) + (v_{\text{sym stretch}} = 1) \)
  - with total \( \Delta v = 1 + 1 = 2 \), so intensity is similar to first overtone.

These transitions are represented using a “Jablonski diagram”:
- For example, for a triatomic with symmetric stretch \( \nu_1 \), bend \( \nu_2 \) and asymmetric stretch \( \nu_3 \): \( (\nu_1, \nu_2, \nu_3) \)
  - \((0,0,1)\) (etc) (etc) (1,0,0) (0,1,0) (1,1,0) (0,0,1) (1,0,0) (0,1,0) (1,1,0)
  - \( v = 0 \) bend sym. str. asym. str. combinations

IR spectrum of \( \text{SO}_2 \)
- symmetric stretch \( \nu_1 \), bend \( \nu_2 \) and asymmetric stretch \( \nu_3 \): \( (\nu_1, \nu_2, \nu_3) \)
  - Absorbance
  - \( \text{SO}_2 \)
**What about bigger molecules?**

- Bigger molecules have more modes of vibration (3N-6).
- Does the spectrum become more and more complicated?
  **YES!**
- Can we understand enough of the spectrum for it to be useful?
  **YES!**
- Some types of vibration have frequencies that remain quite constant ("characteristic frequency") across a wide variety of molecules => LOCAL MODES

**Group Frequencies**

- Just as with orbitals, if the individual vibrations are *not* perfectly matched in energy, the mixing is incomplete
- In cases where the matching is poor, the individual vibration is not mixed much and is almost “pure”

<table>
<thead>
<tr>
<th>Group</th>
<th>Frequency (cm⁻¹)</th>
<th>Group</th>
<th>Frequency (cm⁻¹)</th>
</tr>
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<tbody>
<tr>
<td>O-H stretch</td>
<td>3600</td>
<td>C=O</td>
<td>1700</td>
</tr>
<tr>
<td>N-H stretch</td>
<td>3350</td>
<td>C=C</td>
<td>1650</td>
</tr>
<tr>
<td>C-H stretch</td>
<td>2900</td>
<td>C-C stretch</td>
<td>1200</td>
</tr>
<tr>
<td>C-H bend</td>
<td>1400</td>
<td>C-Cl stretch</td>
<td>700</td>
</tr>
</tbody>
</table>

**IR Spectrum of Acetone**

**Summary**

- There are 3N-6 vibrations in a polyatomic molecule (3N-5 if it is linear)
- There are different types of vibrations, the simplest of which are stretches and bends
- If there are x bonds in a molecule, there are x stretches
- All atoms oscillate at the same frequency in a normal mode
- Many normal modes give rise to characteristic frequencies which are useful for diagnostic chemistry
- Fundamental transitions dominate the IR spectrum. Overtones and combinations are much weaker
- The IR spectrum can be classified using a Jablonski diagram diagram
Next lecture

- The vibrational spectrum of the triatomics and polyatomics (continued)

Week 11 homework

- Work through the units worksheet and the practice problems at the end of the lectures and check your answers with those available online
- Play with the “IR Tutor” in the 3rd floor computer lab and with the online simulations:

Practice Questions

1. In the IR spectrum of an organic molecule, the fundamental and first overtone for a C-H stretch mode appear at 3034 and 5941 cm\(^{-1}\) respectively.
   a) Calculate the harmonic vibrational frequency and anharmonicity constant for this mode (in cm\(^{-1}\)).
   b) Predict the wavenumber for the second overtone
   c) The second overtone appears at 8727 cm\(^{-1}\). Explain any discrepancy between this value and your answer to (b)

2. Methyl bromide has been widely used as a fumigant. However, its use has been banned in the Vienna amendment to the Montreal Protocol because it is an ozone depleting substance. CH\(_3\)Br is also a Greenhouse gas, mainly because of the C-Br stretching vibration, which has a frequency of 611 cm\(^{-1}\).
   a) How many normal modes of vibration does CH\(_3\)Br have?
   b) Which of the schematic representations of CH\(_3\)Br vibrational modes overleaf could not be a normal mode? Explain your answer.

Practice Questions

2. (Continued)
   d) Using the data from part c), estimate the bond dissociation energy for the C – Br bond in CH\(_3\)Br.
   e) The thermodynamic bond dissociation energy for CH\(_3\)Br is 276 kJ mol\(^{-1}\) (which corresponds to 23,070 cm\(^{-1}\)). Provide an explanation for the agreement / disagreement between this value and the value you calculated in part d) of this question.

3. Using the analogy with the s and p orbitals on N, sketch the form of the three N-H stretching modes in NH\(_3\). Which of these modes is IR active?