

Chemistry 2

Lecture 7

Vibrations of Polyatomic Molecules



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 $\Delta v = \pm 1$. For a real molecule, bands with $\Delta v = 1, 2, 3$ are also possible but become increasingly weak.

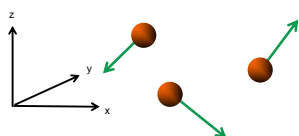
Learning outcomes



- 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 in terms of (strong) fundamental transitions and weaker overtones and combinations

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.

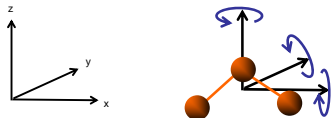


$3N$ degrees of freedom for N atoms

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



3 x translations (along x, y, z) +

3 x rotations (about x, y, z) +

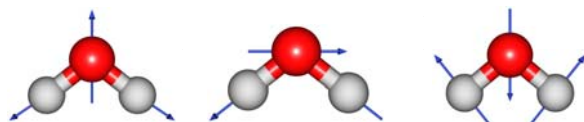
3N-6 vibrations

3N degrees of freedom

Normal Modes of H₂O

Polyatomic molecules can vibrate in many different ways

- H₂O contains 3 atoms so has $3N - 6$ ($3 \times 3 - 6$) = 3 vibrations



symmetric stretch

asymmetric stretch

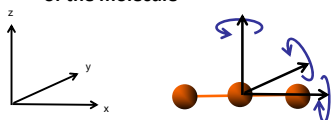
bend

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

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 x translations (along x, y, z) +

2 x rotations (about x, y, z) +

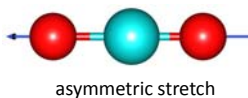
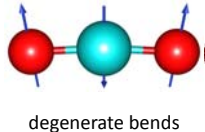
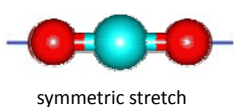
3N-5 vibrations

3N degrees of freedom

Normal Modes of CO₂

Polyatomic molecules can vibrate in many different ways

- CO₂ contains 3 atoms and is linear so has $(3 \times 3 - 5) = 4$ vibrations

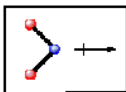
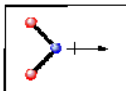


Absorbing IR Light

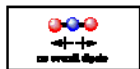
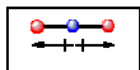
To absorb light, the vibration must produce an oscillating charge

- it is *not* necessary for the molecule to have a dipole moment but one must be produced during the vibration

- H₂O: the symmetric and asymmetric stretches and the bend lead to a change in the dipole



- CO₂: only the asymmetric stretch and the bend leads to a change in the dipole

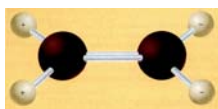


Exercise.....

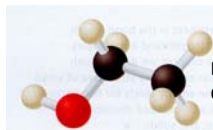
How many vibrational modes do these molecules have?



SF₆



Ethylene, C₂H₄



Ethanol,
C₂H₅OH

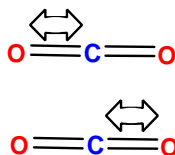
Which molecules can absorb radiation by vibrating?

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

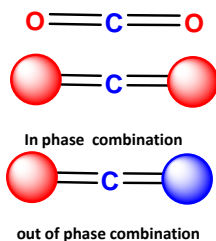
- The individual stretches and bends of different bonds in a molecule are coupled together.



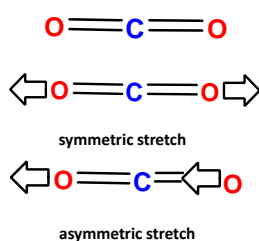
Normal Modes

- 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



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_z are used to σ bond:

Take 'black' lobe as analogous to outward motion and 'white' lobe as analogous to inward motion



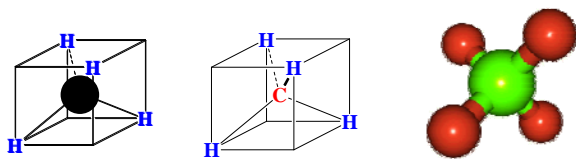
symmetric stretch



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

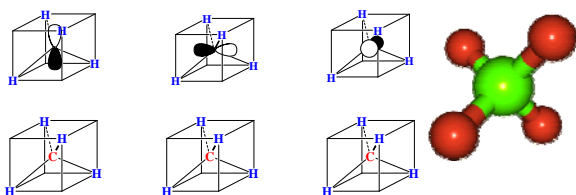


s-orbital

symmetric stretch or "breathing mode"

Normal Modes

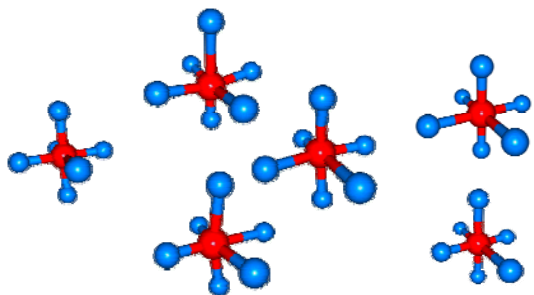
- Stretches are *analogous* to σ bonds: they can be worked out using the atomic orbitals on the central atom which are used for σ bonding
- In methane, C uses its 2s and each of its three 2p orbitals to make σ bonds (" sp^3 ")



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 $3d_{z^2}$

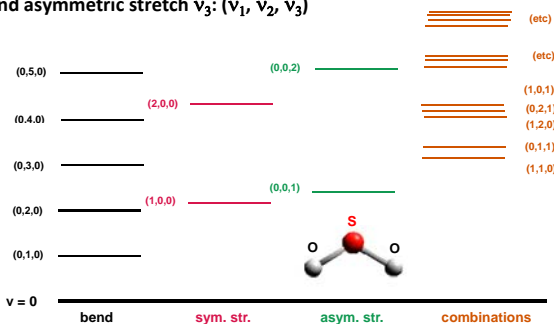


Polyatomic IR Spectroscopy

- 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: $\Delta v_a = 2, \Delta v_a = 3, \dots$
 - $v = 0$ is still the dominant populated state at normal temperature
- PLUS
 - Combinations of vibrations are now possible where several vibrations are simultaneously 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.

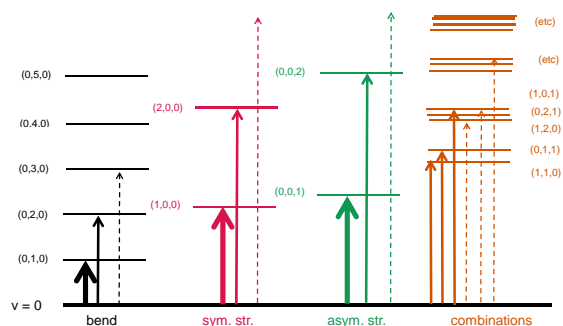
These transitions are represented using a "Jablonski diagram":

- For example, for a triatomic with symmetric stretch ν_1 , bend ν_2 and asymmetric stretch ν_3 : (ν_1, ν_2, ν_3)



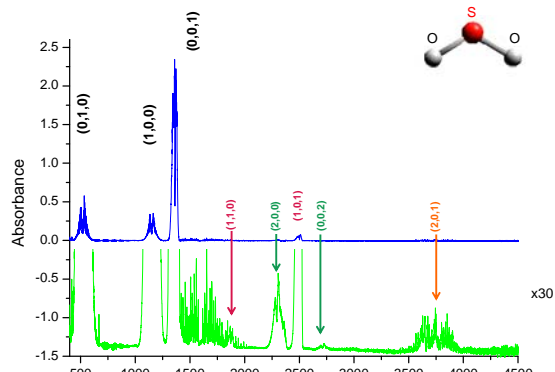
Which transitions will you see in the IR spectrum?

Remember the AHO selection rules!



IR spectrum of SO_2

• symmetric stretch ν_1 , bend ν_2 and asymmetric stretch ν_3 : (ν_1 , ν_2 , ν_3)



What about bigger molecules?

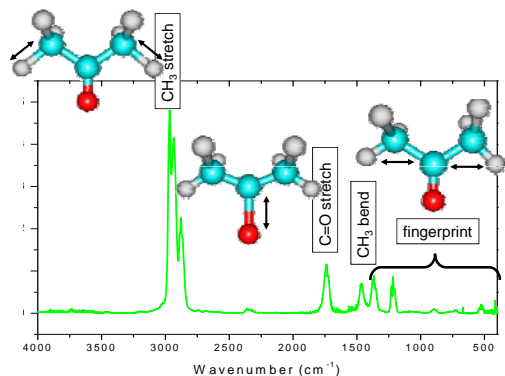
- Bigger molecules have more modes of vibration ($3N-6$).
- Does the spectrum become more and more complicated?
YES!
- Can we understand enough of the spectrum for it to be useful?
YES!
- Some types of vibration have frequencies that remain quite constant ("characteristic frequency") across a wide variety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

Group	Frequency (cm ⁻¹)	Group	Frequency (cm ⁻¹)
O-H stretch	3600	C=O	1700
N-H stretch	3350	C=C	1650
C-H stretch	2900	C-C stretch	1200
C-H bend	1400	C-Cl stretch	700

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

Next lecture

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

Week 11 homework

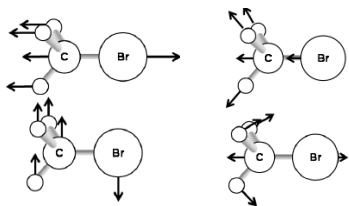
- Work through the units worksheet and the practice problems at the end of the lectures and check your answers with those available online
- Play with the "IR Tutor" in the 3rd floor computer lab and with the online simulations:
<http://assign3.chem.usyd.edu.au/spectroscopy/index.php>

Practice Questions

- 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.
 - Calculate the harmonic vibrational frequency and anharmonicity constant for this mode (in cm^{-1}).
 - Predict the wavenumber for the second overtone
 - The second overtone appears at 8727 cm^{-1} . Explain any discrepancy between this value and your answer to (b)
- 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_3Br is also a Greenhouse gas, mainly because of the C-Br stretching vibration, which has a frequency of 611 cm^{-1} .
 - How many normal modes of vibration does CH_3Br have?
 - Which of the schematic representations of CH_3Br vibrational modes overleaf could **not** be a normal mode? Explain your answer.

Practice Questions

2. (Continued)



- When methyl bromide vibrates in the $(\text{CH}_3) - \text{Br}$ stretching mode it behaves like a pseudo-diatomic molecule because the CH bonds in the methyl group do not vibrate and the whole CH_3 group acts like a big atom. The fundamental transition in the $(\text{CH}_3) - \text{Br}$ stretching mode is found at 611 cm^{-1} . A weak overtone of the same transition is found at 1215 cm^{-1} . Use this information to calculate the harmonic frequency and anharmonicity constant for this mode.

Practice Questions

2. (Continued)
 - d) Using the data from part c), estimate the bond dissociation energy for the C – Br bond in CH₃Br.
 - e) The thermodynamic bond dissociation energy for CH₃Br 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 NH₃. Which of these modes is IR active?
