Chemistry 2

Lecture 8

IR Spectroscopy of Polyatomic Molecles

THE UNIVERSITY OF SYDNEY

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 $\Delta v = \pm 1, 2, 3$ are possible but the overtones ($\Delta v > 1$) are increasingly weak. Combination bands where more than one mode is simultaneously excited are also possible.

Learning outcomes

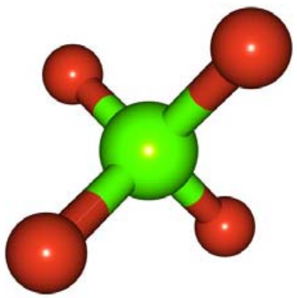
- Be able to pick the vibrational modes in a molecule which are likely to be coupled and those which are likely to be local modes
- Be able to explain the appearance of IR spectra of terms of (strong) fundamental transitions and weaker overtones and combinations
- Be able to use Jablonski diagrams to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

Local Modes

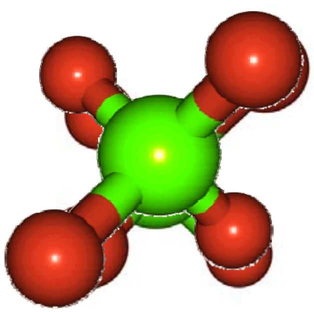
- Although all vibrations in a molecule can couple, for a number of normal modes the bulk of the vibrational amplitude can be found on a small number of atoms.
- This frequently occurs when the natural frequency of an individual vibration is does not closely match that of other vibrations in the molecule

CH_4

2900 cm^{-1}

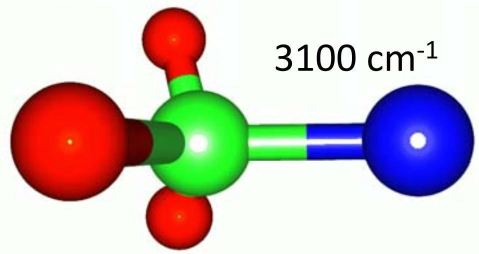


3100 cm^{-1}



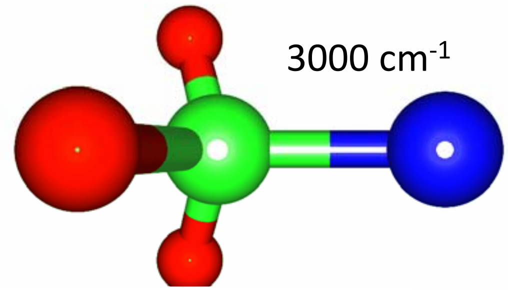
× 3

CH_3Cl

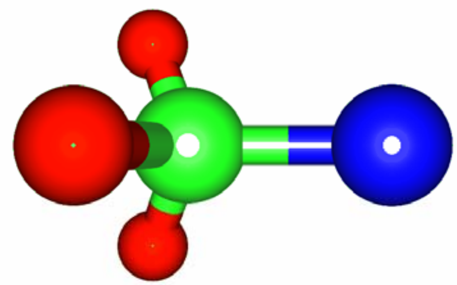


3100 cm^{-1}

× 2



3000 cm^{-1}



700 cm^{-1}

- 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

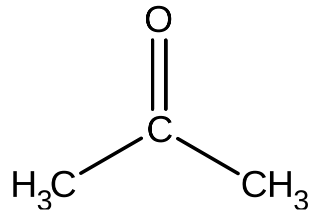
How can you pick local modes?

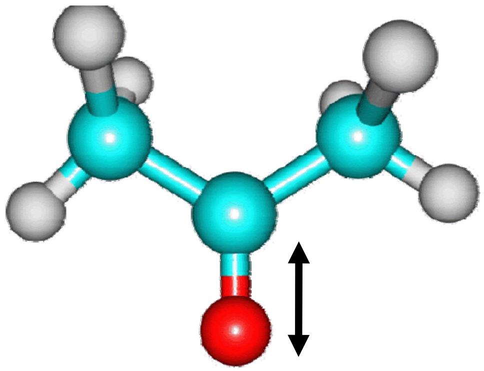
2 main things to look for:

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.

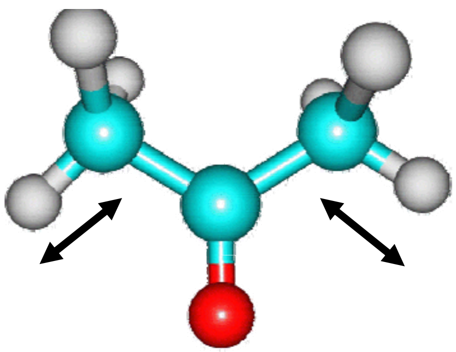
Which vibrations will be local modes?

acetone

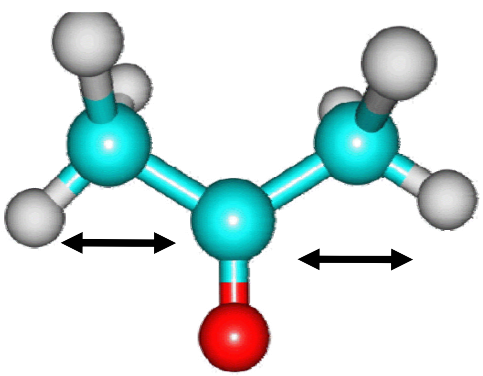




One C-O stretch (1700 – 1730 cm^{-1})

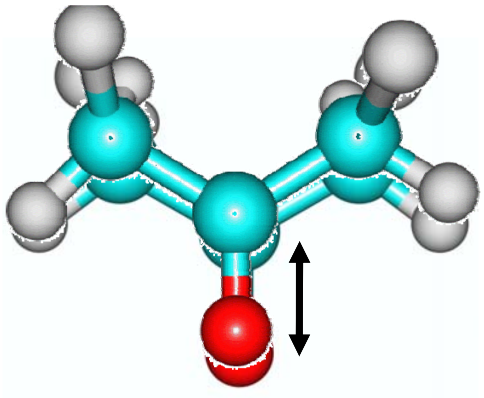


Six C-H stretches (2900 – 3000 cm^{-1}): all mixed with each other

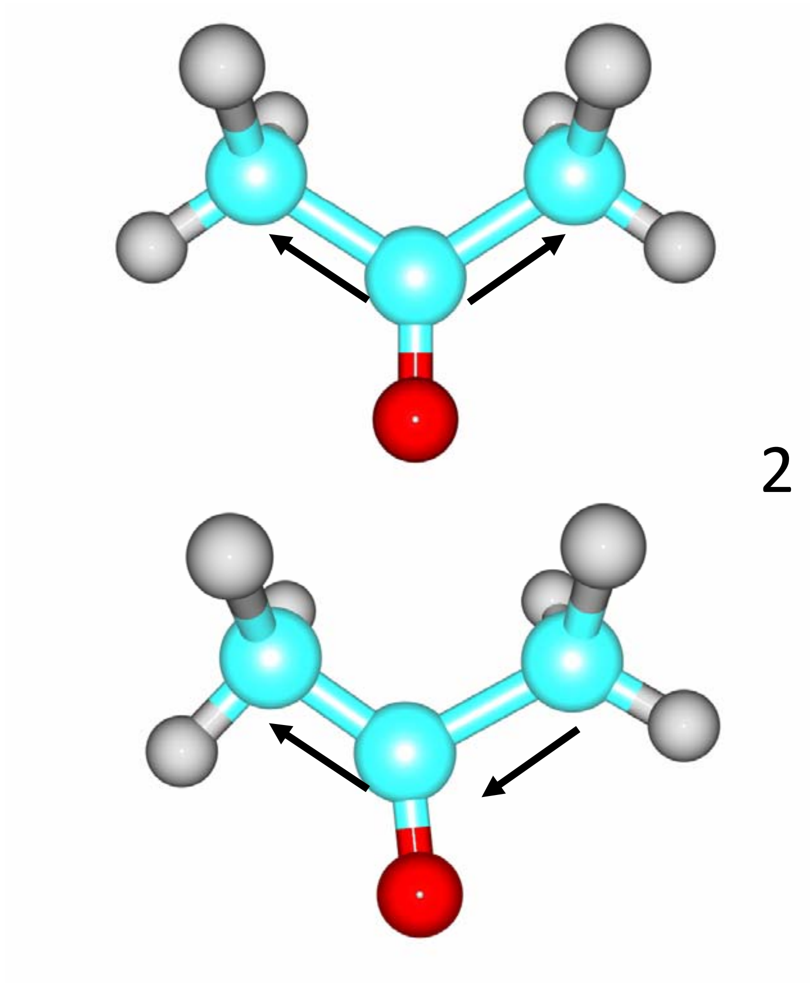


Six C-H bends (1350 – 1450 cm^{-1}): all mixed with each other

Acetone: C-O and C-C stretches

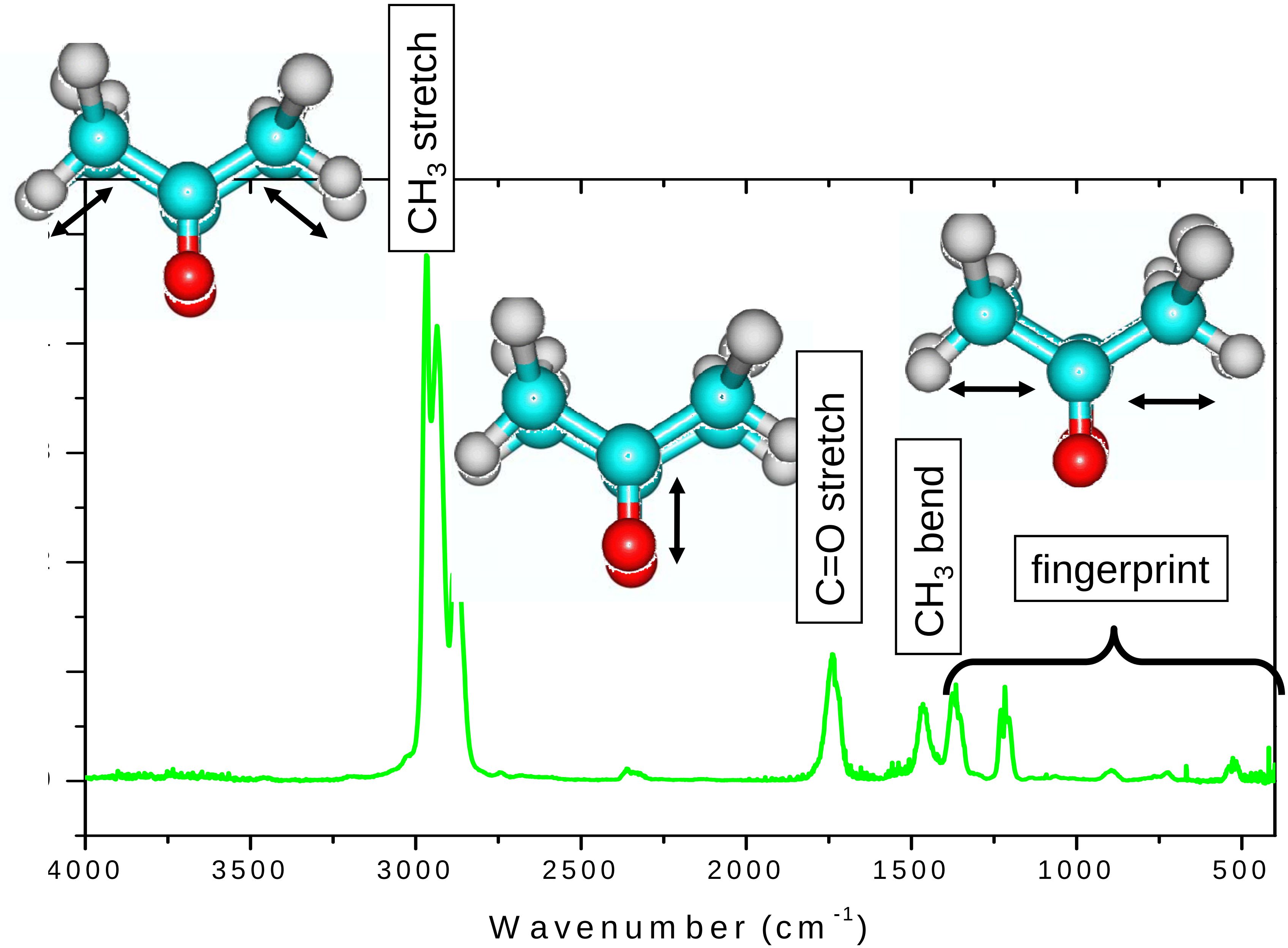


C=O

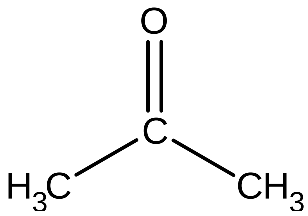


2 C-O

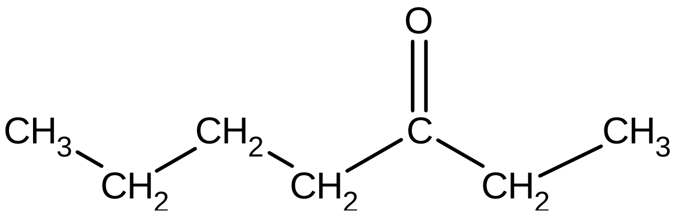
IR Spectrum of Acetone



Which vibrations will be local modes?



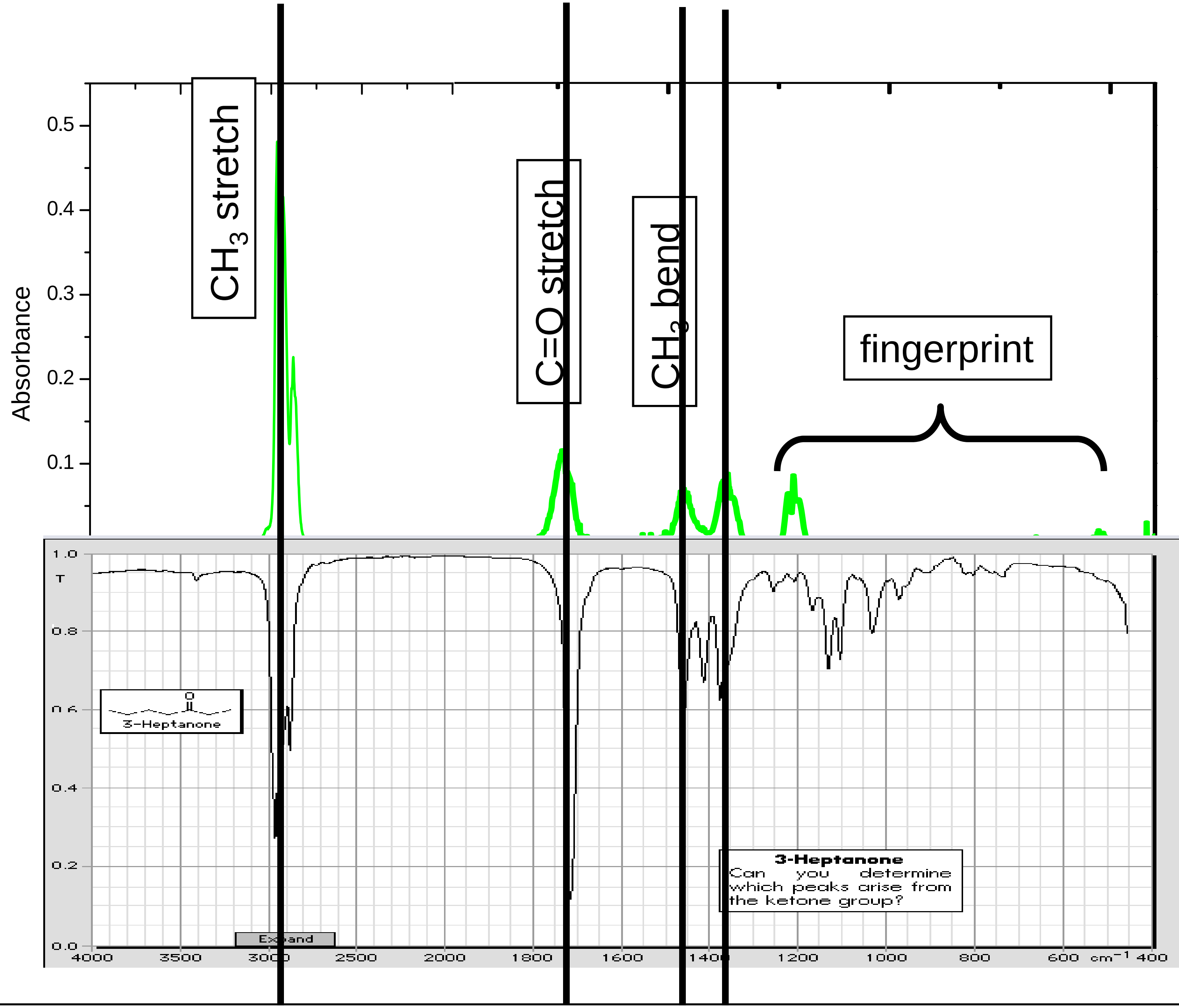
acetone



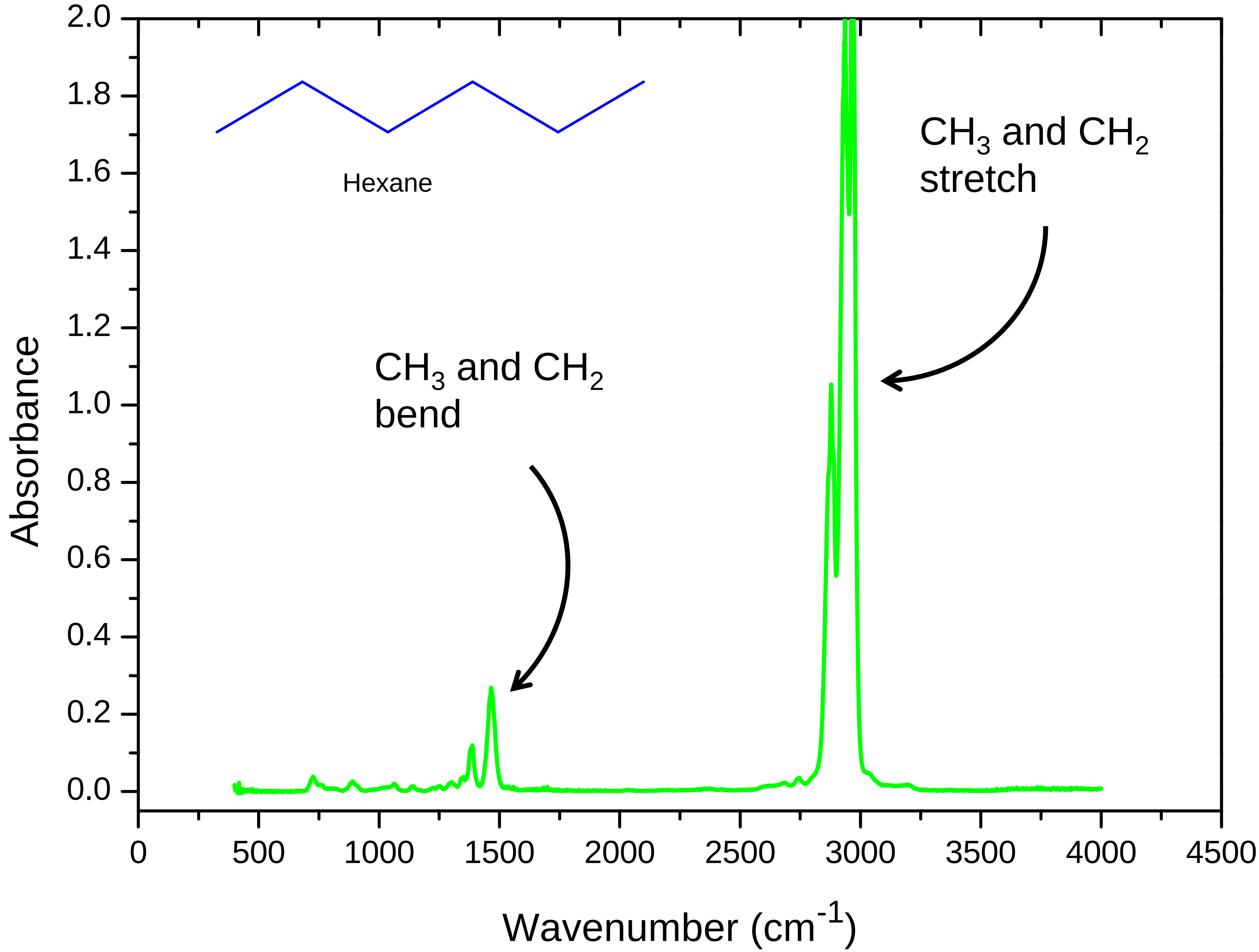
3-heptanone

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

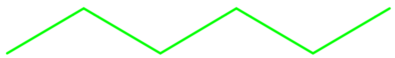
IR Spectrum of acetone and 3-heptanone

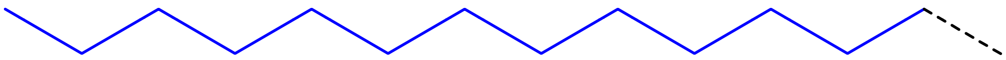


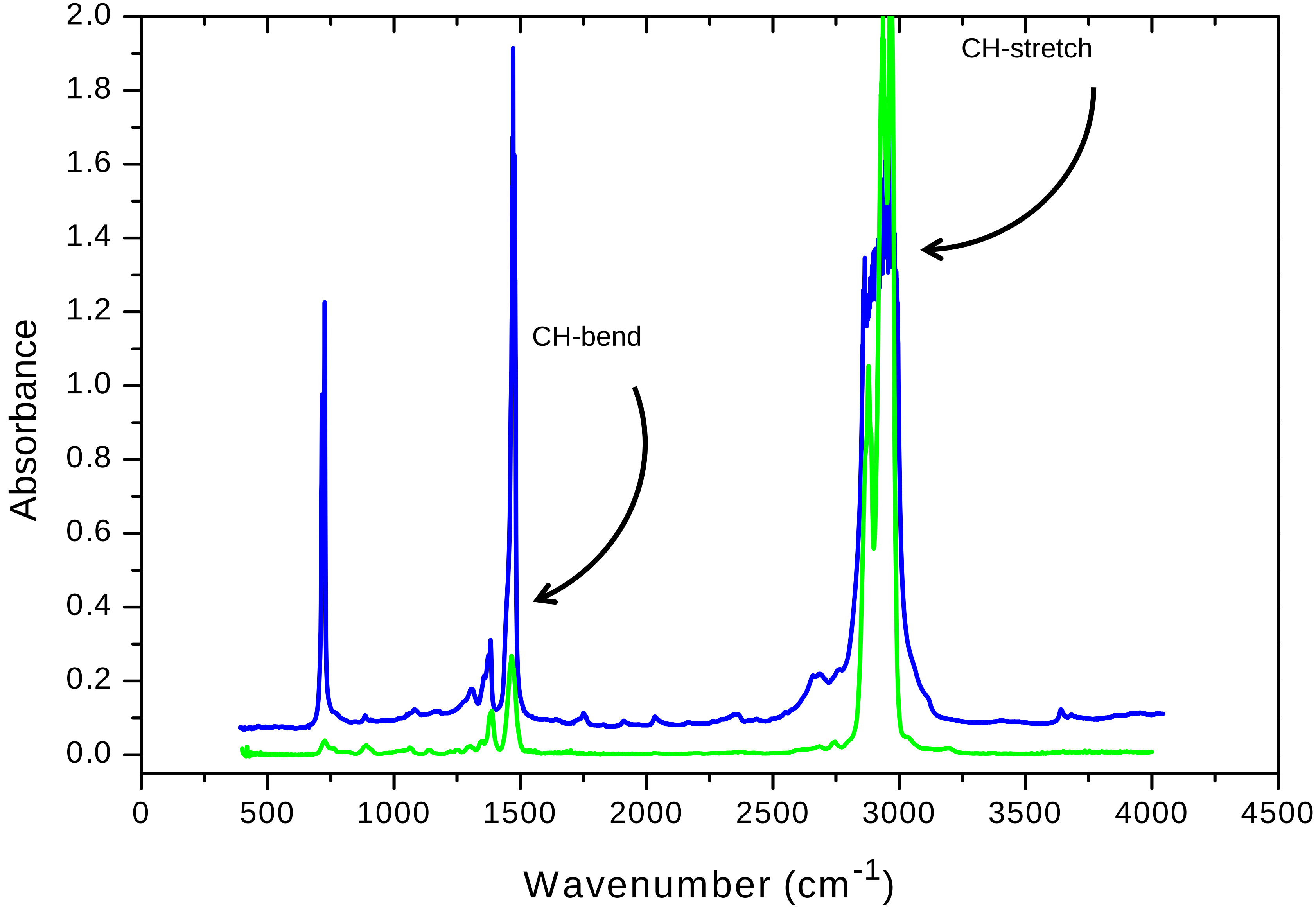
Local vs normal modes in hexane



Hexane vs polyethylene

Hexane 

Polyethylene … 



Jablonski diagrams

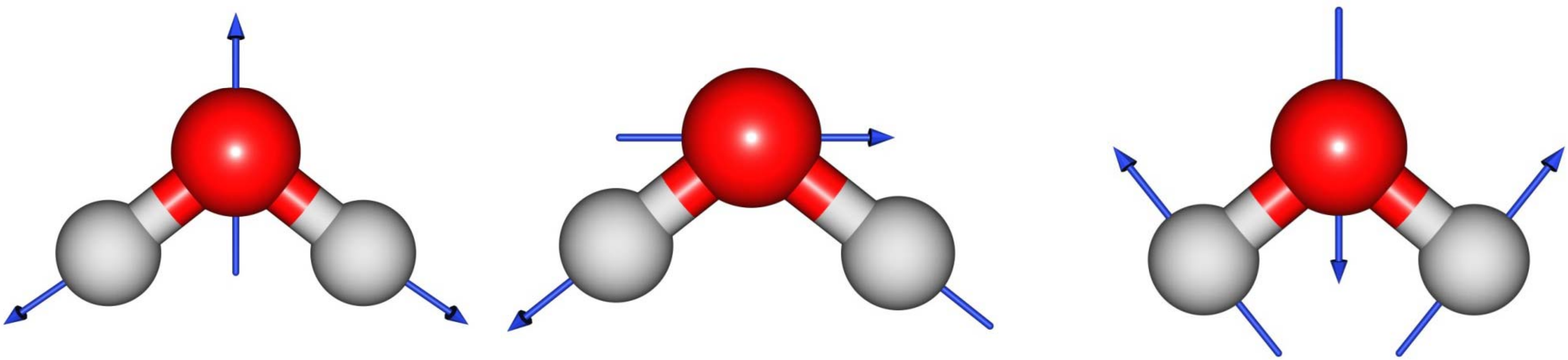
At least for simple molecules, a full analysis of the vibrational spectrum is often possible:

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

Normal Modes of H_2O

Polyatomic molecules can vibrate in many different ways

- **H_2O contains 3 atoms so has 3N – 6 (3 × 3 – 6) = 3 vibrations**
- **Each is IR active**



symmetric stretch
ν_1 = 3657 cm^{-1}

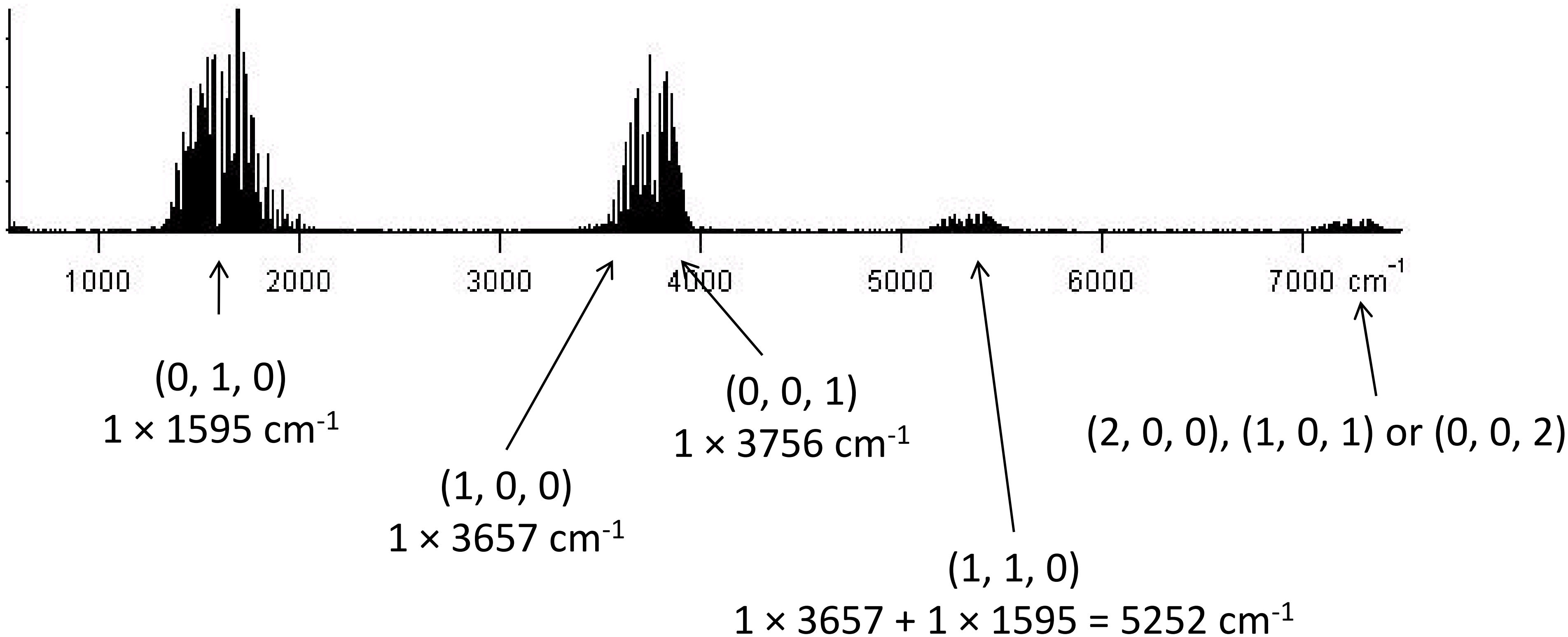
asymmetric stretch
ν_3 = 3756 cm^{-1}

bend
ν_2 = 1595 cm^{-1}

Vibrational Spectrum of H_2O

Polyatomic molecules can vibrate in many different ways

- ν_1 = 3657 cm^{-1}, ν_2 = 1595 cm^{-1} , ν_3 = 3756 cm^{-1} ,
- Label excitations as (v_1, v_2, v_3)
- As first approximation, neglect effect of anharmonicity on energies

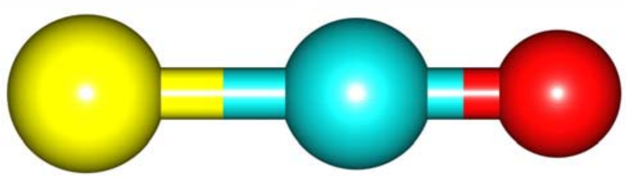


- Overtones carry on into visible with decreasing absorption

Vibrational Spectrum of OCS

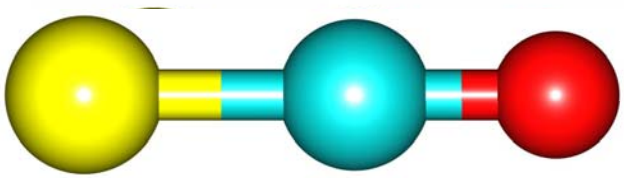
Polyatomic molecules can vibrate in many different ways

- **Linear so 3N-5 = 4 vibrations**
- **Unlike CO_2, the C=O and C=S natural frequencies are different leading to incomplete mixing:**



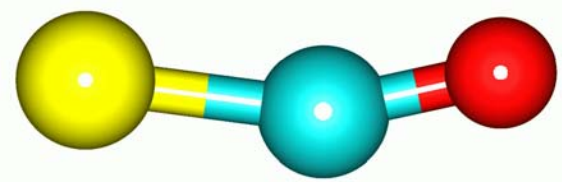
CO stretch

$\nu_1 = 2062\ cm^{-1}$



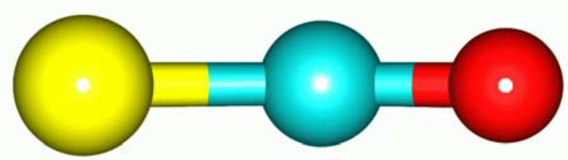
CS stretch

$\nu_3 = 859\ cm^{-1}$

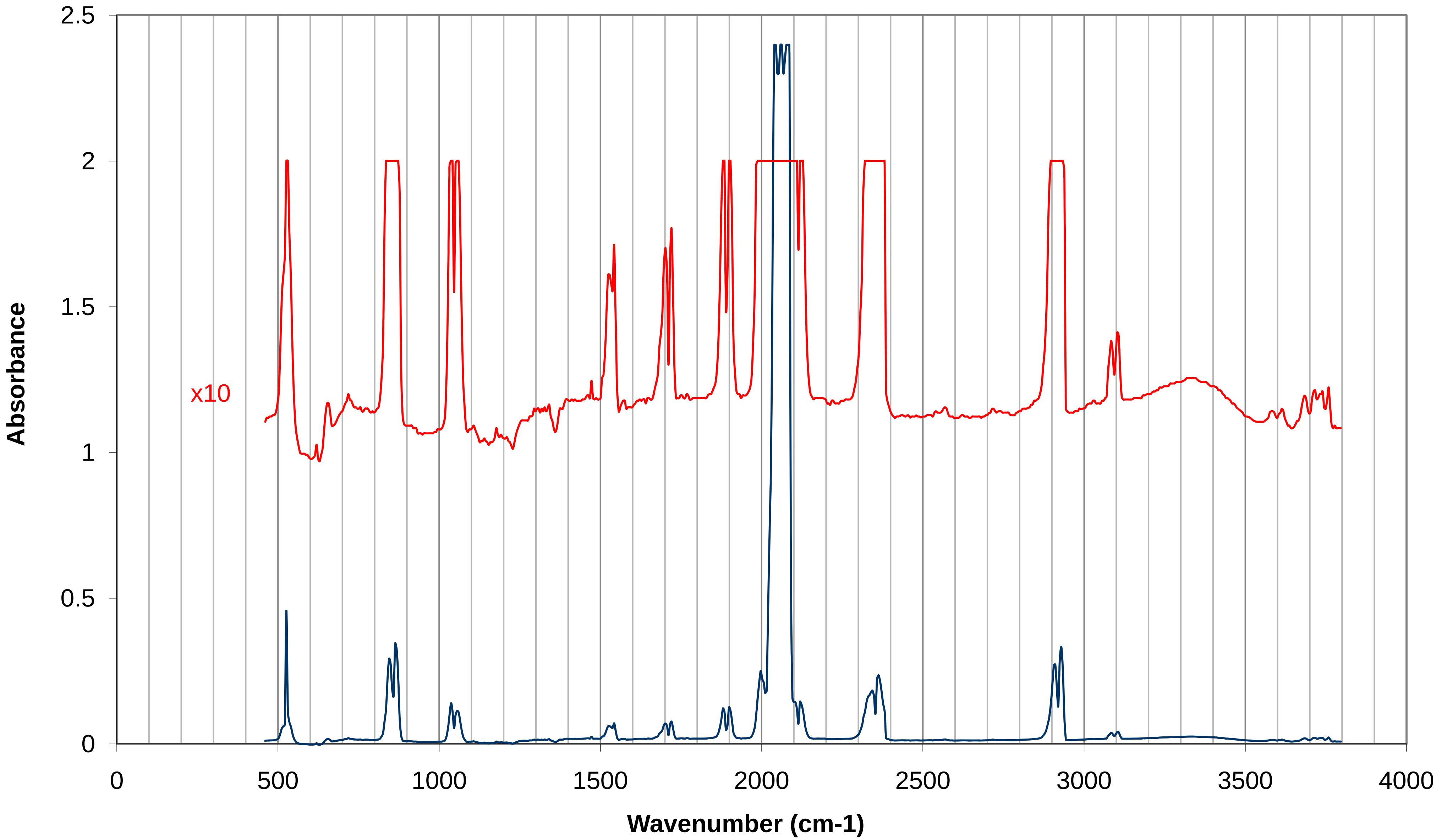


two degenerate bends

$\nu_2 = 520\ cm^{-1}$



Vibrational Spectrum of OCS



Next lecture

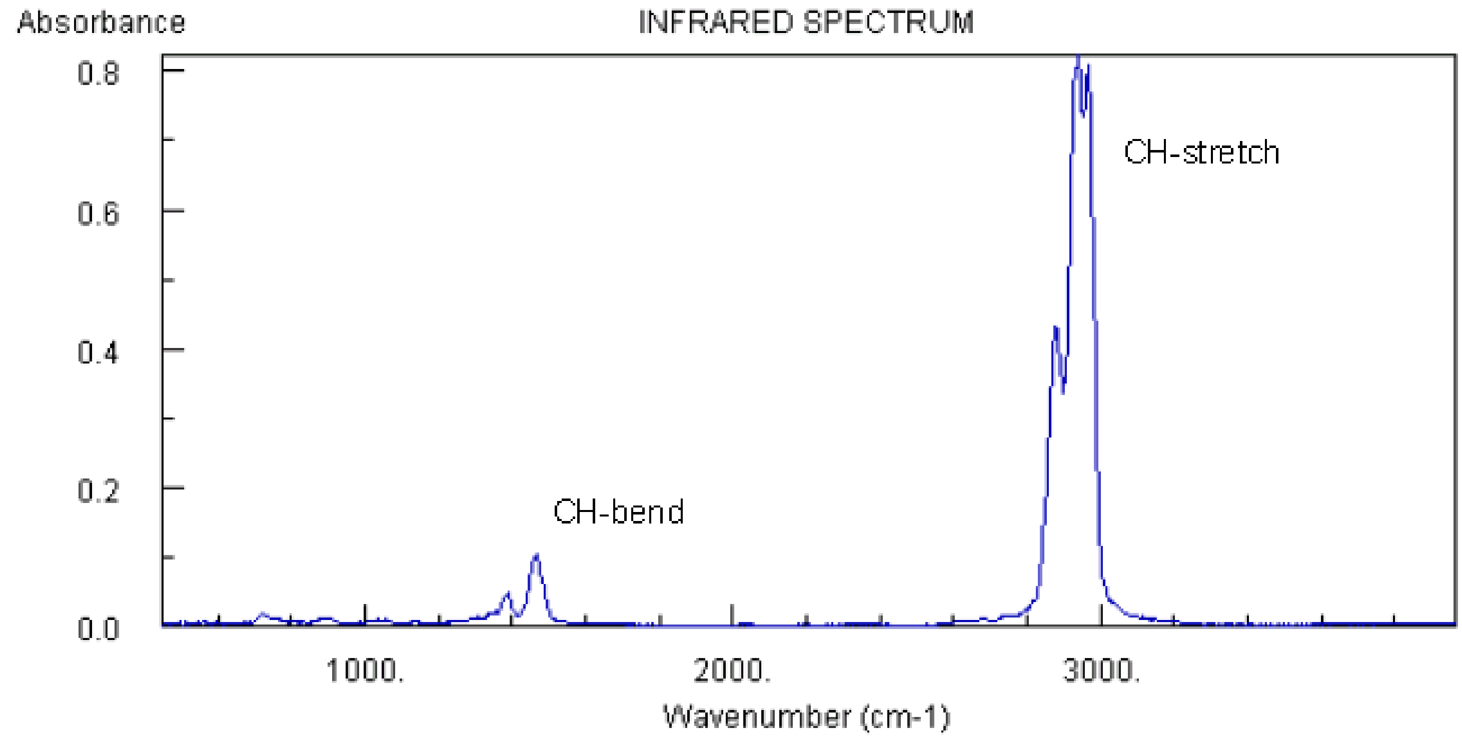
- Raman spectroscopy

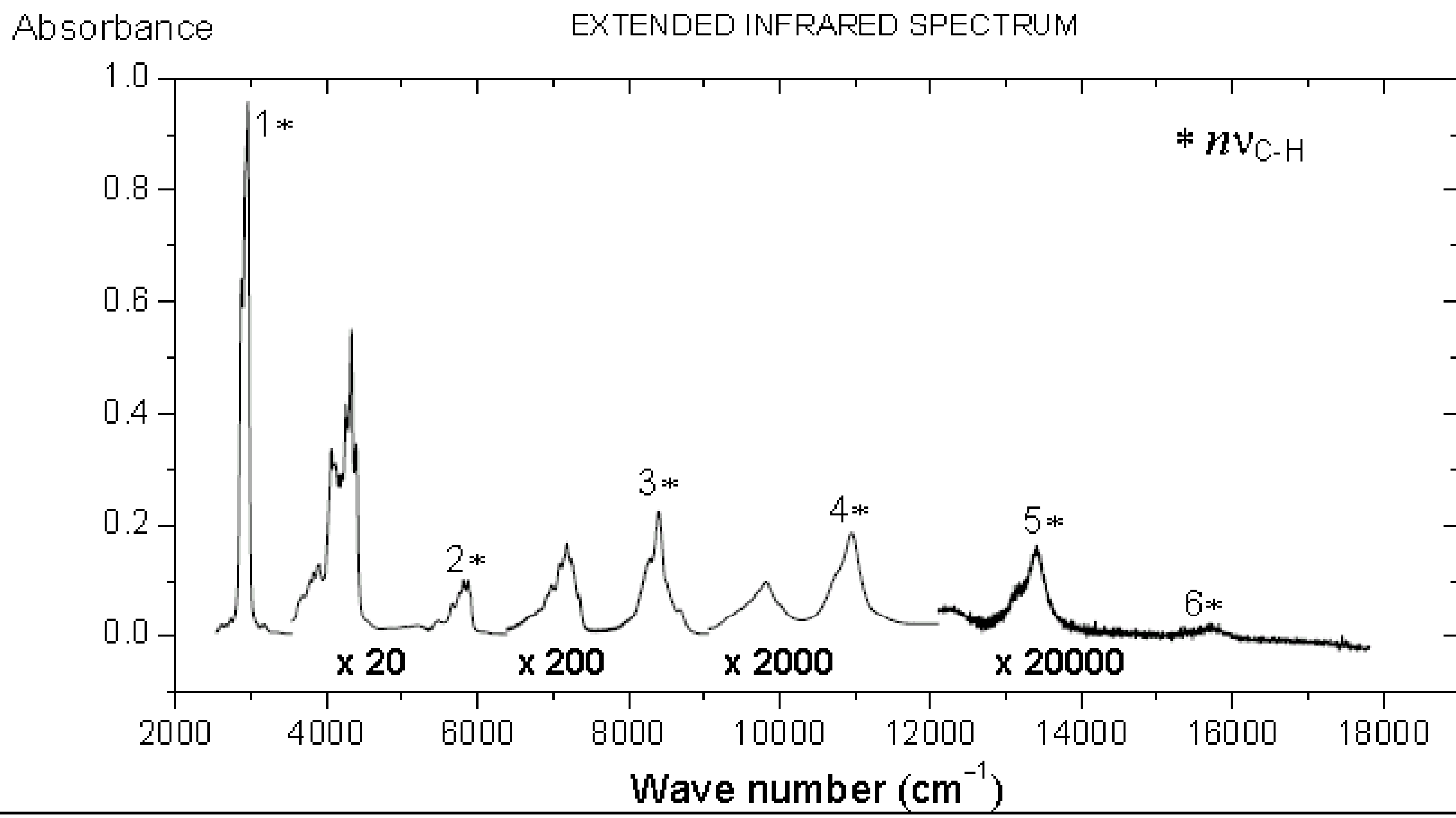
Week 12 tutorial and homework

- 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 (C_6H_{14}) 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 $v = 0 \rightarrow 5$ transition marked "5*"), from the bottom spectrum, is ν = 13401 cm^{-1}. Calculate the harmonic constant, ω_e, and the anharmonicity constant, $\omega_e x_e$ for the CH bond.
   c) Estimate the bond dissociation energy, $D_{0,}$ 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)


Absorbance
INFRARED SPECTRUM
0.8
0.6
0.4
0.2
0.0
CH-stretch
CH-bend
1000.
2000.
3000.
Wavenumber (cm-1)


Absorbance
EXTENDED INFRARED SPECTRUM
1.0
0.8
0.6
0.4
0.2
0.0
1*
2*
3*
4*
5*
6*
* $n\nu_{C-H}$
x 20
x 200
x 2000
x 20000
2000
4000
6000
8000
10000
12000
14000
16000
18000
Wave number (cm^{-1})