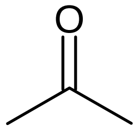
Chapter 3. Infrared spectroscopy

vibrational transitions



- which transitions?
  - wavelength and intensity, $\bar{\nu}$
- how many vibrations
- what happens if we change the molecule?
  - substituent effects on $\bar{\nu}$

- prediction of $\bar{\nu}$

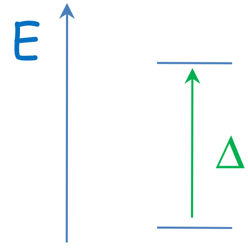
Reading:
Pavia
Chapter 2

1. General

- range of radiation: ≈ 2.5 – 25 μm: λ usually used as x-axis on old IR spectra

  ≈ 4000 – 400 cm^{-1}: $\bar{\nu}$ used as x-axis on new IR spectra

  $\bar{\nu} = 1/\lambda$: advantage: $\bar{\nu}$ directly proportional to E
- absorption leads to increased amplitude of molecular vibrations



E

vibrationally excited state

ΔE: absorbed energy, quantized

vibrational ground state of a molecule

ΔE is quantized, but again no line spectrum due to rotational levels X

Question: How large is the energy gap needed (let's say at 3000 cm^{-1}) and what does that imply for the population of the two states?

$$E = h\nu = hc\bar{\nu} = 6.6 \cdot 10^{-34}\,Js \cdot 3 \cdot 10^{8}\,m/s \cdot 3000\,cm^{-1} \cdot 100\,cm/m = 5.9 \cdot 10^{-20}\,J$$

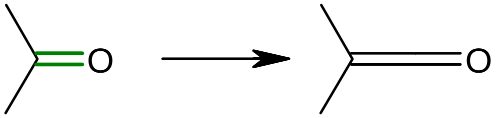
$$\frac{N_u}{N_l} = e^{-\frac{\Delta E}{kT}} = e^{-\frac{5.9 \cdot 10^{-20}\,J}{1.38 \cdot 10^{-23}\,J/K \cdot 298\,K}} = 5.9 \cdot 10^{-7} \approx \frac{1}{2{,}000{,}000}$$

For 400 cm^{-1}?

2. Selection rules

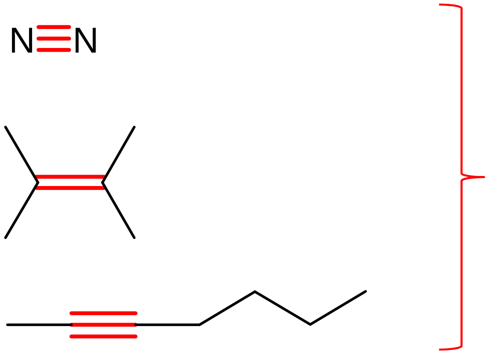
- govern which transitions are allowed, which forbidden
- allowed transition is observed
- forbidden transition is either not observed or very weak

- most important: dipole moment has to change with time



: changes
: vibration is IR active

for symmetric or pseudo-symmetric bonds:



: “no” change
: vibration is IR inactive
(but Raman active)

3. Spectral regions

- shown are the band positions of ***stretching vibrations*** of functional groups

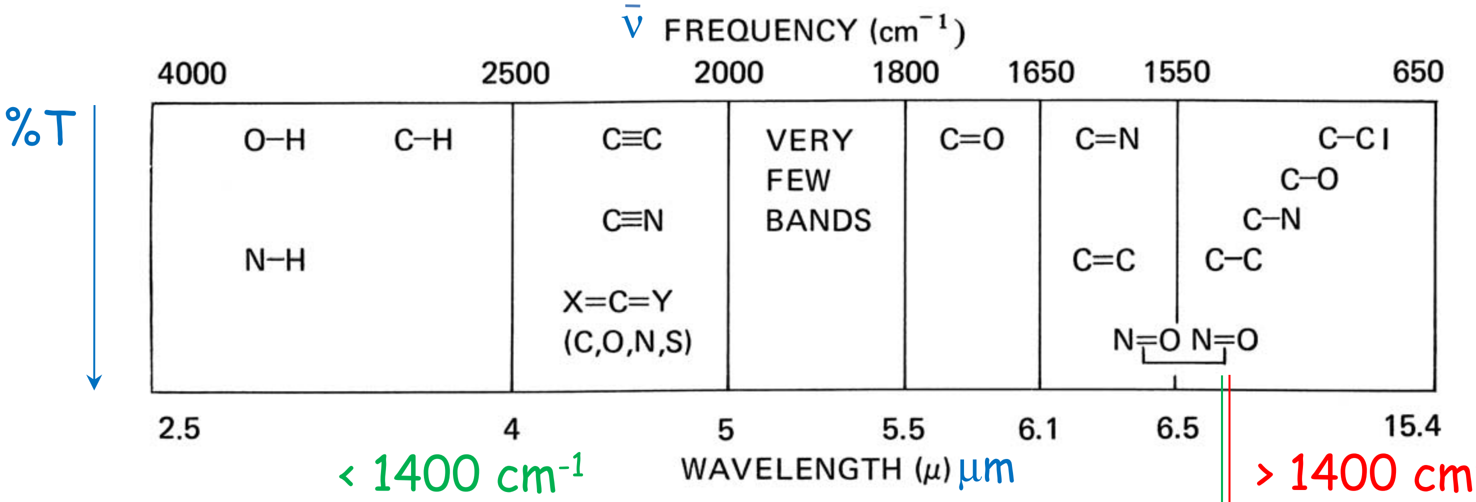


Fig. 2.2

< 1400 cm^{-1}

← functional group region →

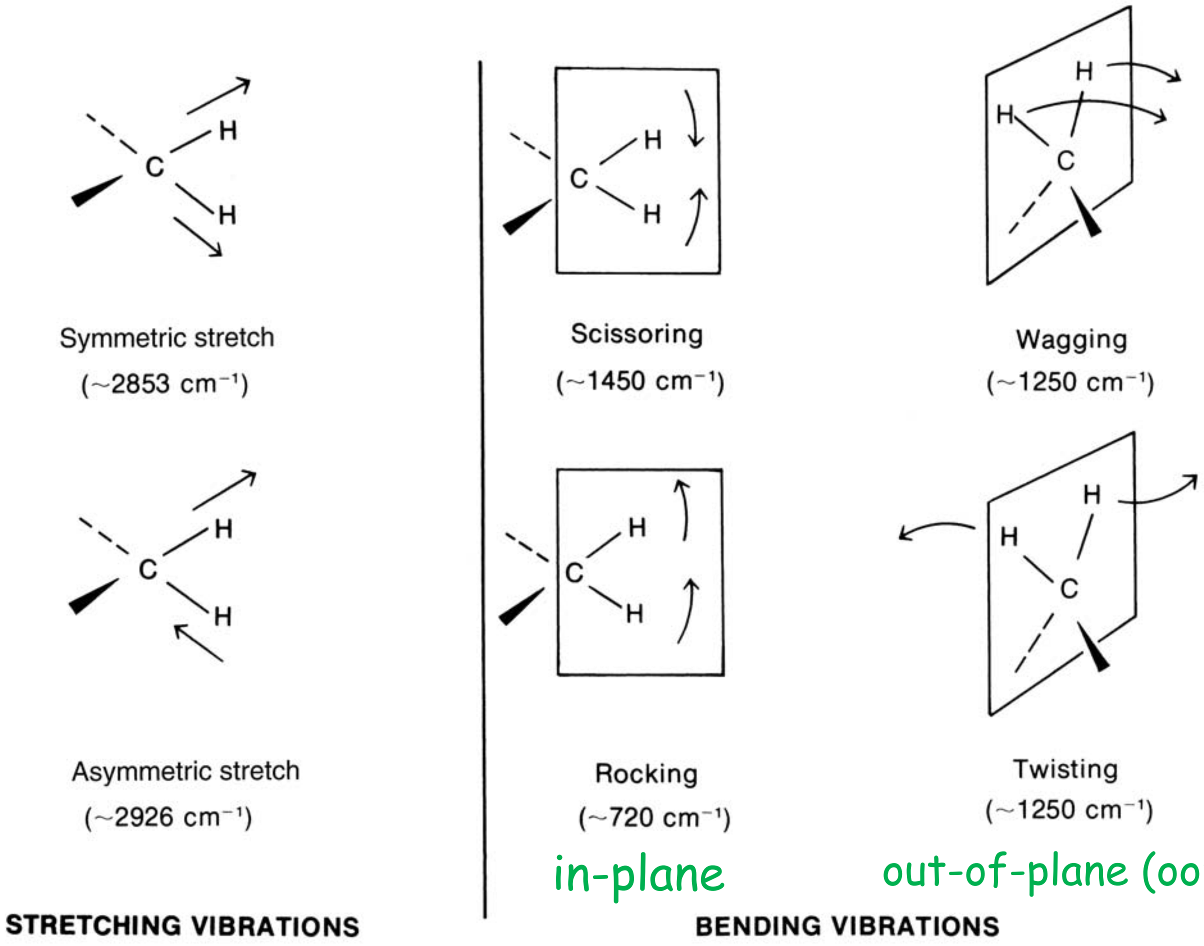
> 1400 cm^{-1}

fingerprint region

- the functional group region has more or less localized vibrations
- the fingerprint region has vibrations of the whole skeleton
- the fingerprint region is only interpreted
  - to seek or confirm additional information from the functional group region
  - for aromatic and alkene substitution patterns

4. Types of vibration

- fundamental absorptions: stretching (ν) and bending (δ)



in-plane

out-of-plane (oop) : HCH plane

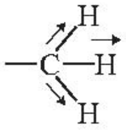
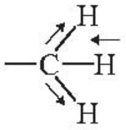
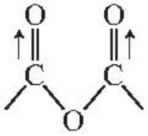
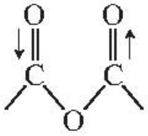
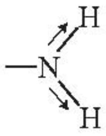
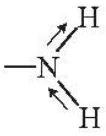
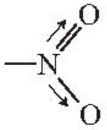
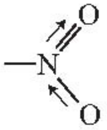
bending terminology is not important for us

given as: ν(C-H)

$\delta(CH_2)$

4. Types of vibration continued

- symmetric and asymmetric variations of a vibration give rise to two bands where only one should be

Symmetric Stretch ν_s	**Asymmetric Stretch** ν_{as}
 ~2872 cm^{-1}	 ~2962 cm^{-1}
 ~1760 cm^{-1}	 ~1800 cm^{-1}
 ~3300 cm^{-1}	 ~3400 cm^{-1}
 ~1350 cm^{-1}	 ~1550 cm^{-1}

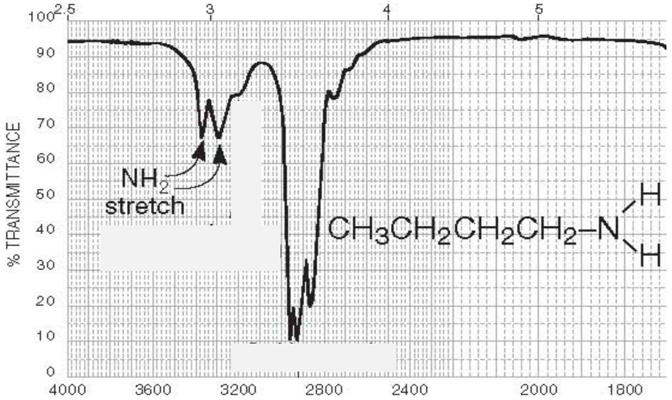


Fig. 2.58

2 ν(N-H) does ***not*** imply 2 different N-H bonds!

4. Types of vibration continued

- besides fundamental absorptions we know
  - overtones: multiples of a fundamental (low intensity)

    $2\bar{\nu}$, $3\bar{\nu}$
  - combination bands: two frequencies couple

    $\bar{\nu}_1 + \bar{\nu}_2$
  - difference bands: two frequencies couple

    $\bar{\nu}_1 - \bar{\nu}_2$
  - Fermi-resonance bands: fundamental couples with overtone or combination band because of accidental degeneracy of $\bar{\nu}$

    : the two bands split

    : important in aldehydes
- all of these lead to more bands in the IR spectrum than expected
- recall: less bands than expected due to symmetry

$\nu(C\equiv C)$ is not IR active!

4. Types of vibration continued

- more bands in the IR spectrum than expected due to overtones…
- less bands than expected due to symmetry

⇒ How many bands do we expect?

\# of vibrational modes for a molecule with n atoms:

3n – 5 for linear molecules

3n – 6 for non-linear molecules

What are these 5 or 6?

Examples: linear: H-C≡C-H

$n = 4 \Rightarrow 3 \cdot 4 - 5 = 7$ fundamentals (less observed)

non-linear: $H_2C{=}CH_2$

$n = 6 \Rightarrow 3 \cdot 6 - 6 = 12$ fundamentals (less observed)

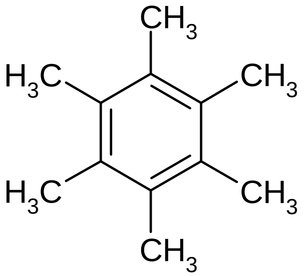
- out of 3n–6 we expect: stretch: n-1

  bend: n-2

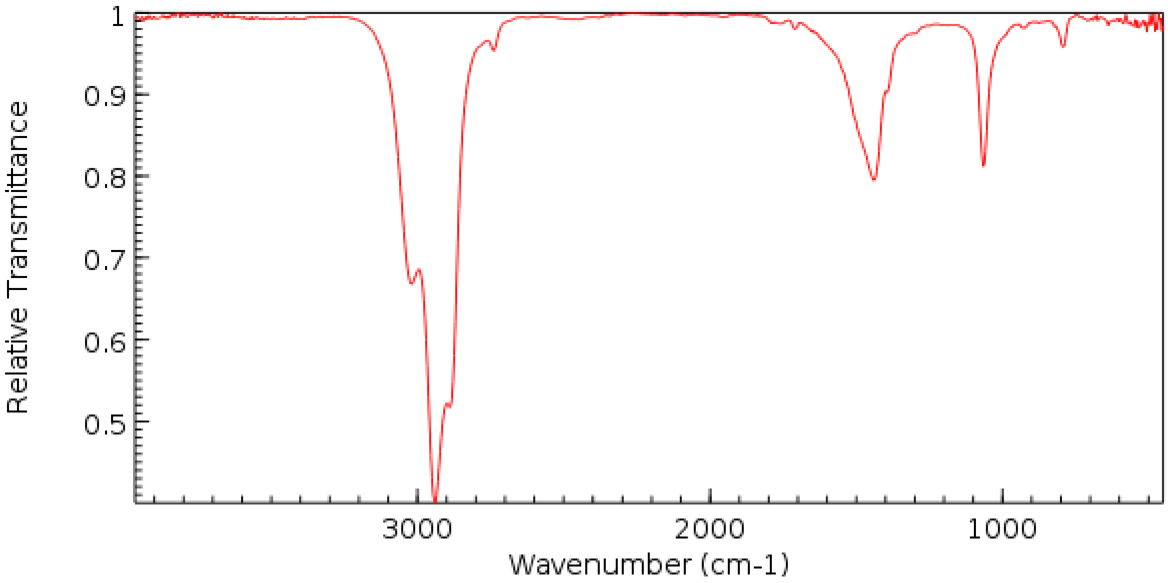
  torsion: n-3

4. Types of vibration continued

- the effect of symmetry on the # of observed fundamentals can be huge:



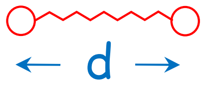
$C_{12}H_{18} \Rightarrow$ 3n-6 = 84 vibrations, but observed are only about 10



http://webbook.nist.gov/chemistry

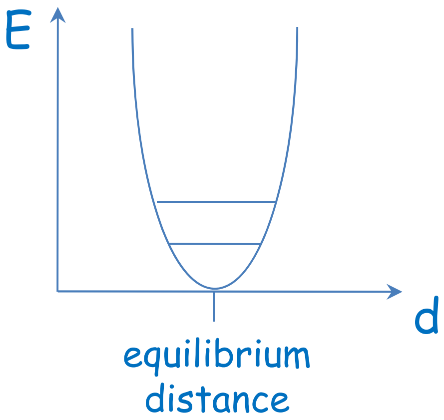
5. The stretching vibration

- a stretching absorption $\bar{\nu}$ can be easily estimated with the help of Hooke's law
- assumption: two atoms of a bond are particles on a spring



⇒ vibration is described with a harmonic oscillator

⇒ E depends on the stiffness of the spring and the attached masses



needed observed

$E \sim \bar{\nu}$

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

force constant [dyn/cm]

reduced mass [g]

$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$

⇒ larger K (stiffer bond) ⇒ larger $\bar{\nu}$

C≡C	C=C	C-C	
2150	1650	1200	cm^{-1}

larger m ⇒ smaller $\bar{\nu}$

C-H	C-C	C-O	
3000	1200	1100	cm^{-1}

5. The stretching vibration continued

- for a workable equation, convert masses with Avogadro's # into atomic masses and consider π and c

$$\bar{\nu} = 4.12\sqrt{\frac{K}{\mu}}$$

examples

C-C

$$K = 5 \cdot 10^5 \text{ dyn/cm}$$

$$\mu = \frac{12 \cdot 12}{12 + 12} = 6$$

$$\bar{\nu} = 4.12\sqrt{\frac{5 \cdot 10^5}{6}} = 1189\, cm^{-1}$$

experimental ~ 1200 cm^{-1}

C=C

$$K = 10 \cdot 10^5 \text{ dyn/cm}$$

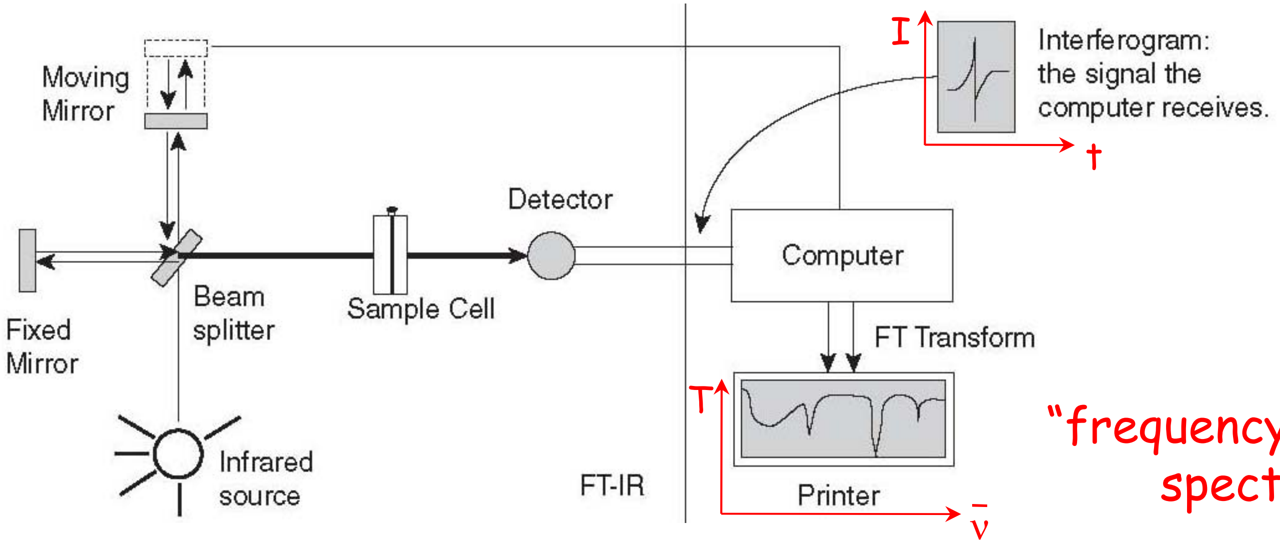
$$\mu = 6$$

$$\bar{\nu} = 4.12\sqrt{\frac{10 \cdot 10^5}{6}} = 1682\, cm^{-1}$$

experimental ~ 1650 cm^{-1}

6. Spectrometer

- Dispersive IR
  - similar to UV-Vis spectrophotometer
  - lamp: heated wire, detector: thermocouple
  - uses reference beam to account for atmospheric absorptions   Like?
- Fourier-transform (FT)IR

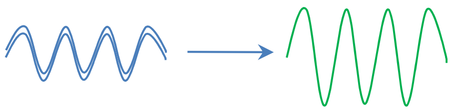


"time-domain" spectrum

"frequency-domain" spectrum

Fig. 2.3

⇒ both mirrors at same distance: constructive interference



otherwise: progressively destructive interference until

Advantage? Disadvantage?

7. Materials

- Central question: Where does the material absorb?
- samples: - gas: in gas-cell

  - liquid: between plates
  - solution: in liquid-cell

  - solid: as pellet or suspension

crystal windows required:

- AgCl: to 360 cm^{-1}
  not brittle
- CaF_2: to 1100 cm^{-1}
  for acids
- KBr: to 400 cm^{-1}
  cheap $60 for one

KBr

nujol

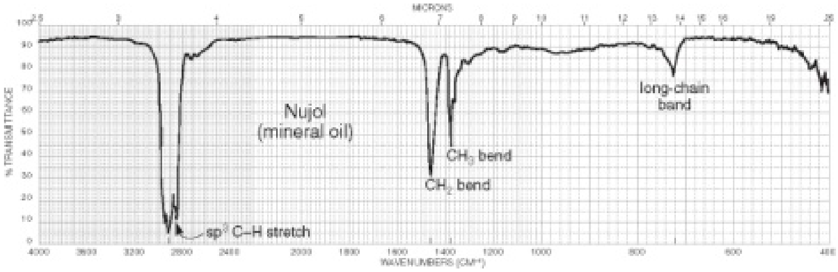
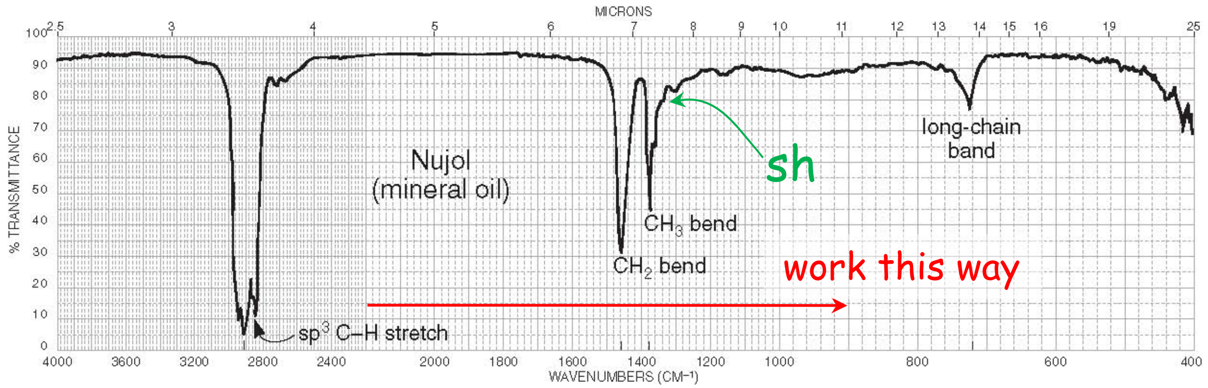


Fig. 2.8

http://bucksci.thomasnet.com
http://www.technosearchinstruments.com

8. Spectrum

- IR spectra are often not published
- x-y data of the extrema are reported instead
  - intensities are given relatively, are integrated into the list of bands



s strong
m medium
w weak
sh shoulder

Fig. 2.8

Info from this spectrum reported:

2900 cm^{-1} s ν(C-H) sp^3
1460 cm^{-1} m $\delta(CH_2)$
1380 cm^{-1} m $\delta(CH_3)$
720 cm^{-1} w $\delta(CH_2)$ ("long chain band" is additional structural information)

- Finally: IR spectra are often not linear! Check carefully for $\bar{\nu}$