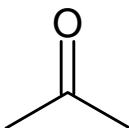


# Chapter 3. Infrared spectroscopy

## vibrational transitions

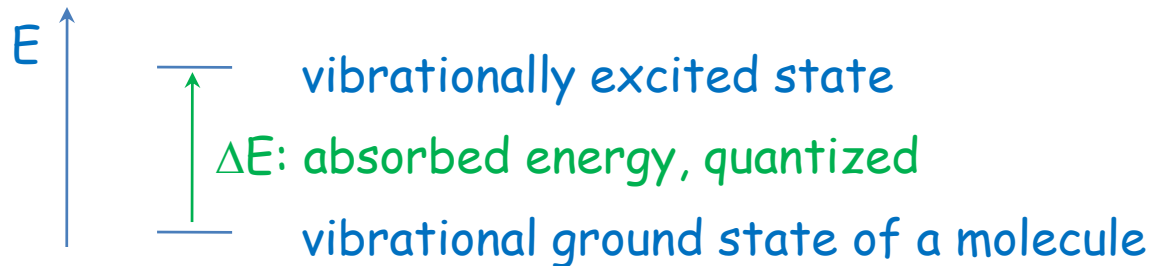


- which transitions?  
wavelength and intensity,  $\bar{\nu}$
- how many vibrations
- what happens if we change the molecule?  
substituent effects on  $\bar{\nu}$
  
- prediction of  $\bar{\nu}$

Reading:  
Pavia  
Chapter 2

# 1. General

- range of radiation:  $\approx 2.5 - 25 \mu\text{m}$ :  $\lambda$  usually used as x-axis on old IR spectra  
 $\approx 4000 - 400 \text{ cm}^{-1}$ :  $\bar{\nu}$  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



$\Delta E$  is quantized, but again no line spectrum due to rotational levels X

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

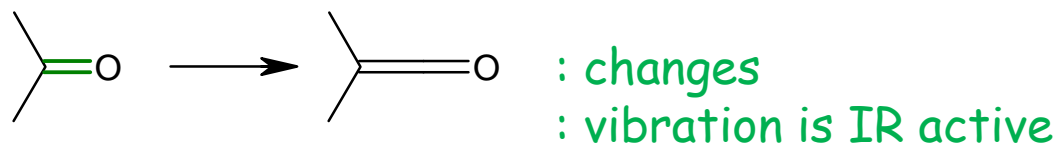
$$E = h\nu = hc\bar{\nu} = 6.6 \cdot 10^{-34} \text{ Js} \cdot 3 \cdot 10^8 \text{ m/s} \cdot 3000 \text{ cm}^{-1} \cdot 100 \text{ cm/m} = 5.9 \cdot 10^{-20} \text{ J}$$

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

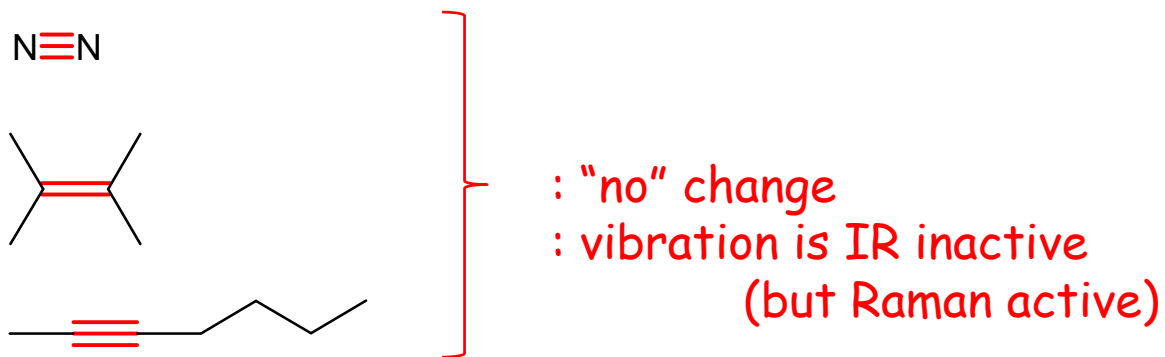
For  $400 \text{ cm}^{-1}$ ?

## 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

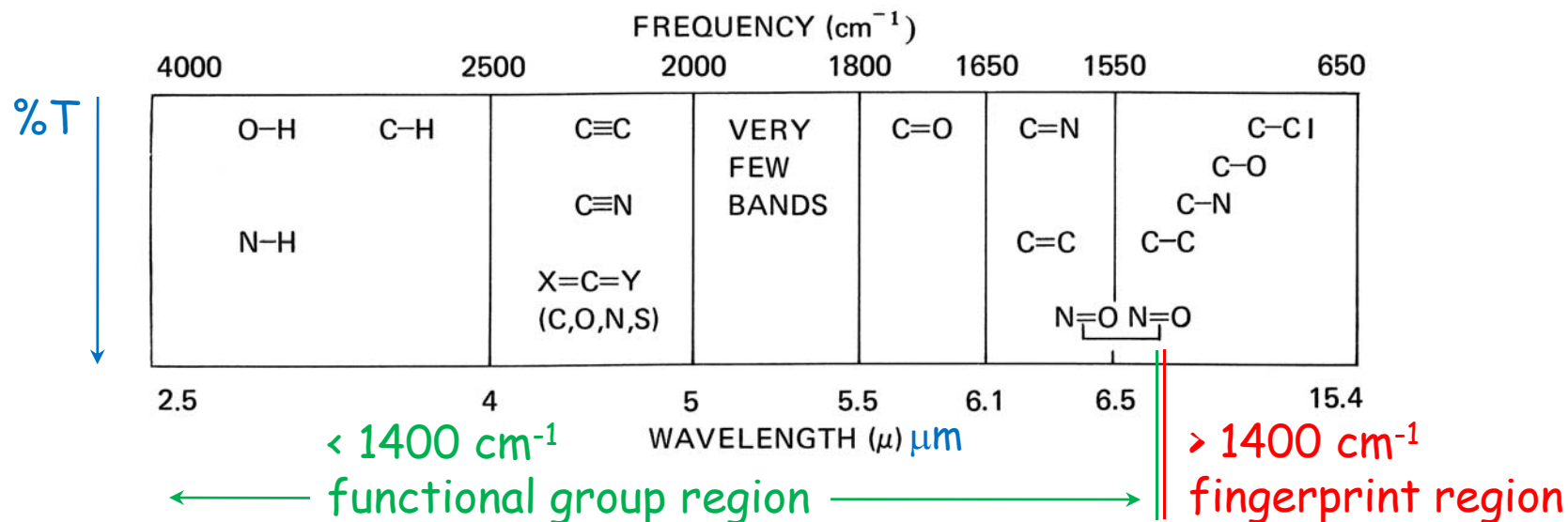


for symmetric or pseudo-symmetric bonds:



### 3. Spectral regions

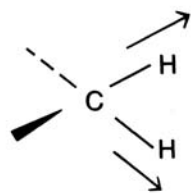
- shown are the band positions of *stretching vibrations* of functional groups



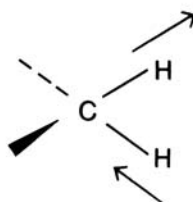
- the functional group region has more or less localized vibrations
- the fingerprint region has vibrations of the whole skeleton
- the fingerprint region is only interpreted
  - to seek or confirm additional information from the functional group region
  - for aromatic and alkene substitution patterns

# 4. Types of vibration

- fundamental absorptions: stretching ( $\nu$ ) and bending ( $\delta$ )

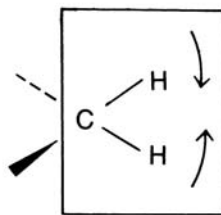


Symmetric stretch  
( $\sim 2853 \text{ cm}^{-1}$ )

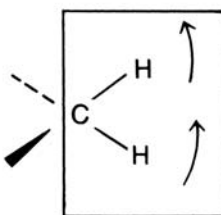


Asymmetric stretch  
( $\sim 2926 \text{ cm}^{-1}$ )

**STRETCHING VIBRATIONS**

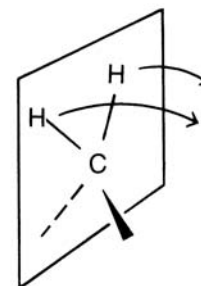


Scissoring  
( $\sim 1450 \text{ cm}^{-1}$ )

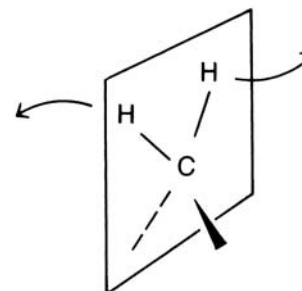


Rocking  
( $\sim 720 \text{ cm}^{-1}$ )

in-plane



Wagging  
( $\sim 1250 \text{ cm}^{-1}$ )



Twisting  
( $\sim 1250 \text{ cm}^{-1}$ )

out-of-plane (oop) : HCH plane

bending terminology is not important for us

**BENDING VIBRATIONS**

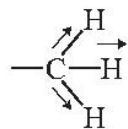
given as:  $\nu(\text{C-H})$

$\delta(\text{CH}_2)$

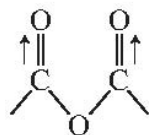
## 4. Types of vibration continued

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

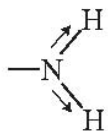
Symmetric Stretch  $\nu_s$



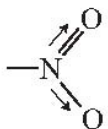
$\sim 2872 \text{ cm}^{-1}$



$\sim 1760 \text{ cm}^{-1}$

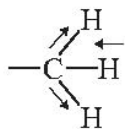


$\sim 3300 \text{ cm}^{-1}$

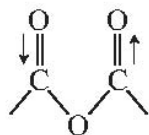


$\sim 1350 \text{ cm}^{-1}$

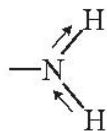
Asymmetric Stretch  $\nu_{as}$



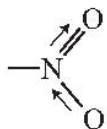
$\sim 2962 \text{ cm}^{-1}$



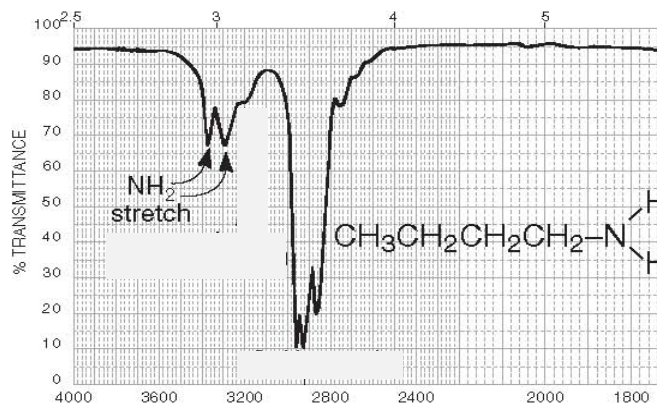
$\sim 1800 \text{ cm}^{-1}$



$\sim 3400 \text{ cm}^{-1}$



$\sim 1550 \text{ cm}^{-1}$



$2 \nu(\text{N-H})$  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



## 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:  $\text{H}-\text{C}\equiv\text{C}-\text{H}$

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

non-linear:  $\text{H}_2\text{C}=\text{CH}_2$

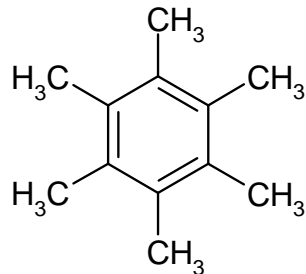
$n = 6 \Rightarrow 3 \cdot 6 - 6 = 12$  fundamentals (less observed)

- out of  $3n-6$  we expect: stretch:  $n-1$   
bend:  $n-2$   
torsion:  $n-3$

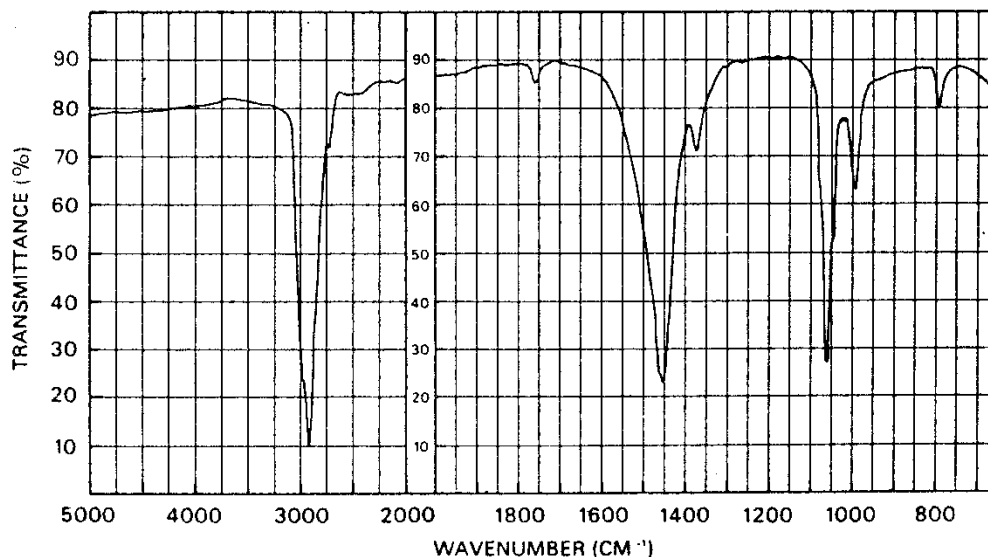


## 4. Types of vibration continued

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

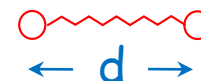


$C_{12}H_{18} \Rightarrow 3n-6 = 84$  vibrations, but observed are only about 10



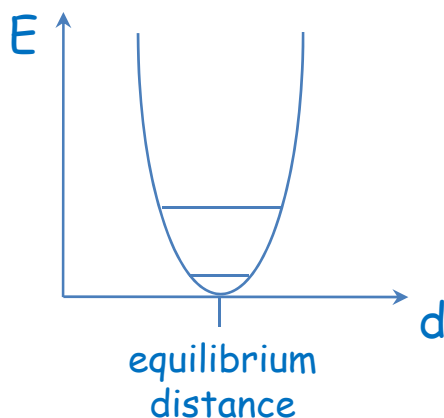
## 5. The stretching vibration

- 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  $\bar{\nu}$

$C \equiv C$	$C = C$	$C - C$	
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  $\pi$  and  $c$

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

### examples

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

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

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

experimental  
~ 1200  $\text{cm}^{-1}$

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

$$\mu = 6$$

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

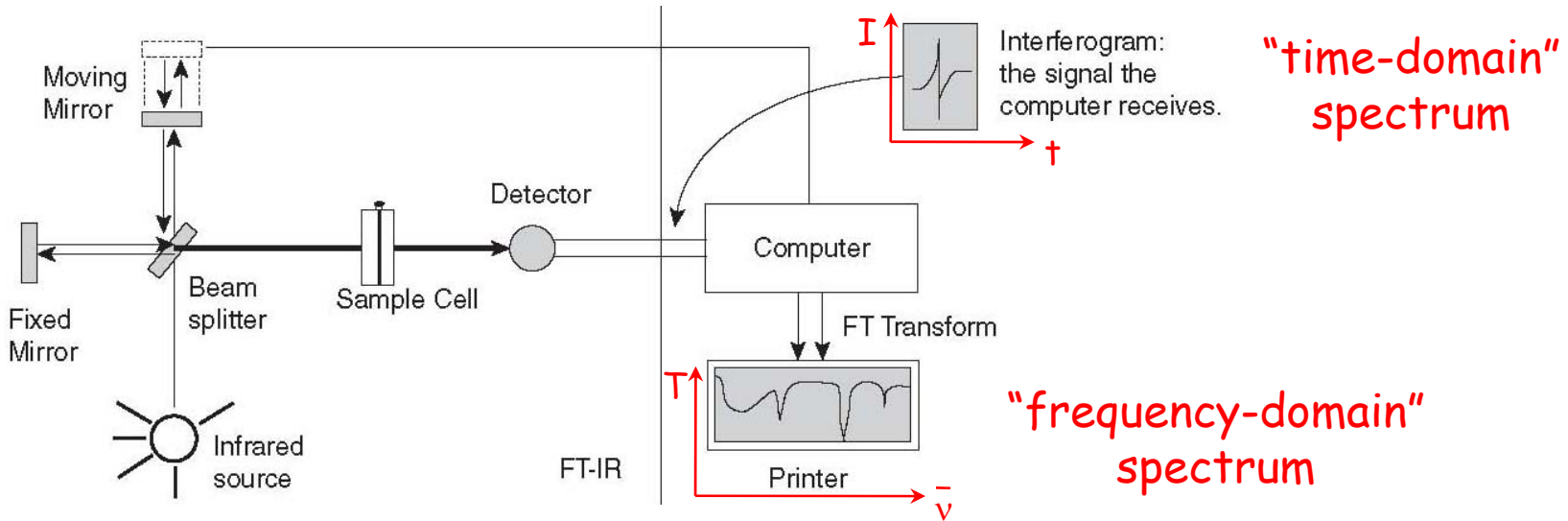
experimental  
~ 1650  $\text{cm}^{-1}$


# 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**



⇒ 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  $360\text{ cm}^{-1}$

not brittle

- **CaF<sub>2</sub>:** to  $1100\text{ cm}^{-1}$

for acids

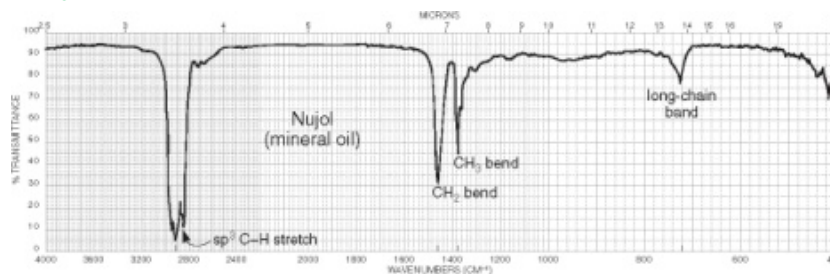
- **KBr:** to  $400\text{ cm}^{-1}$

cheap

**KBr**



**nujol**

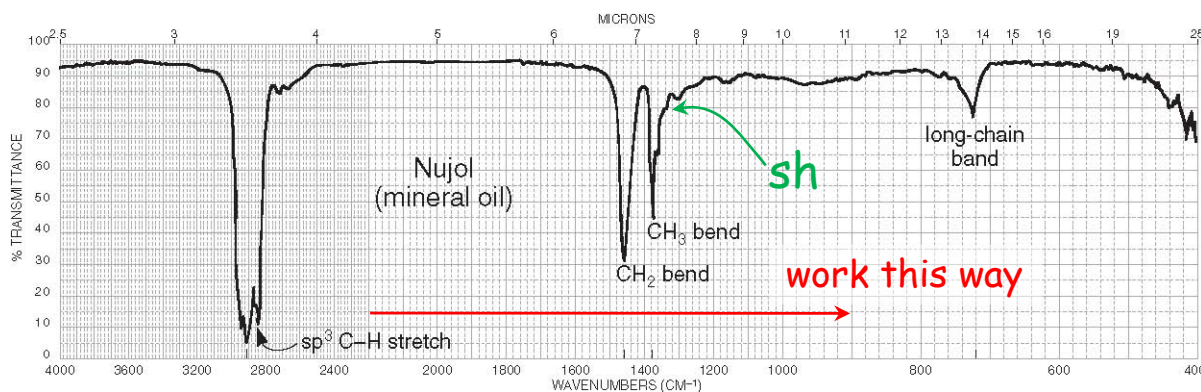


<http://bucksci.thomasnet.com>

<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

Info from this spectrum **reported**:

2900 cm<sup>-1</sup> s  $\nu(\text{C-H})$  sp<sup>3</sup>

1460 cm<sup>-1</sup> m  $\delta(\text{CH}_2)$

1380 cm<sup>-1</sup> m  $\delta(\text{CH}_3)$

720 cm<sup>-1</sup> w  $\delta(\text{CH}_2)$  ("long chain band" is additional structural information)

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