**CHEM 222 section 01**

Notes may change
a little before class

**LECTURE #08**

Thurs., Sept.27, 2007

## Lecture topics & readings

**Today's class**

- IR spectroscopy (sections 12.6-12.15)

**Before next class**

- read section on IR spectroscopy in Bruice
- read Lehman's Operation section on IR

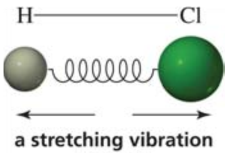
**Next class**

- finish IR
- start mass spectrometry (12.1-12.5)

**Helpful website for spectroscopy topics: Michigan State University**
**http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm#contnt**

## 12.7-12.15 Infrared (IR) Spectroscopy
## = a VIBRATIONAL spectroscopy

*cf UV/Vis = an electronic spectroscopy*



**Vibrational energy levels**

- correlate with allowed vibrational frequencies
- separated by $\Delta E$ matching IR radiation
  - frequency range: 600 – 4000 $cm^{-1}$

**Wavenumbers ($cm^{-1}$)** = # waves per cm
= frequency unit used for IR

$$\bar{\nu}\,(\mathrm{cm}^{-1}) = \frac{10^4}{\lambda\,(\mu\mathrm{m})}$$ *because* $1\ \mu m = 10^{-4}\ cm$

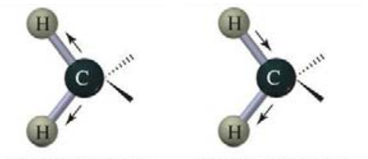
**Higher wavenumbers = larger "spring" force constant**
stronger bond *OR* lighter atoms

***C–N stretch:*** *1100* $cm^{-1}$ ⇨ $\lambda = 9.1\ \mu m$
***C=N stretch:*** *1600* $cm^{-1}$
***C≡N stretch:*** *2200* $cm^{-1}$

***C–H stretch:*** *3000* $cm^{-1}$
***C–D stretch:*** *2200* $cm^{-1}$

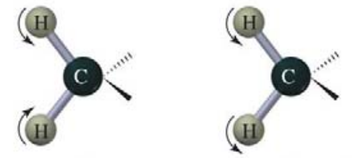
## Typical vibrational modes in complex molecules

### Stretching vibrations

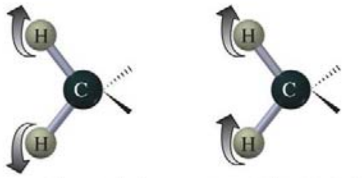


symmetric stretch  asymmetric stretch

### Bending vibrations



symmetric in-plane bend (scissor)  asymmetric in-plane bend (rock)



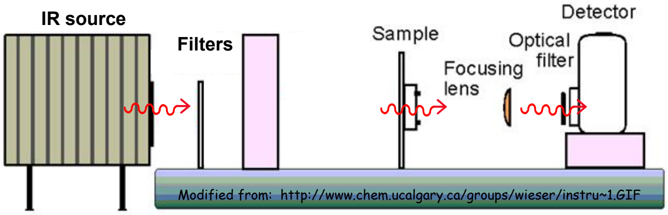
symmetric out-of-plane bend (twist)  asymmetric out-of-plane bend (wag)

If a vibration leads to a change in molecule's dipole moment, it is ***IR active*** :

Larger dipole moment change
⇨ more intense absorption
⇨ larger peak in spectrum

*See the textbook website for stretching/bending tutorial…*

## Measuring an IR absorption spectrum



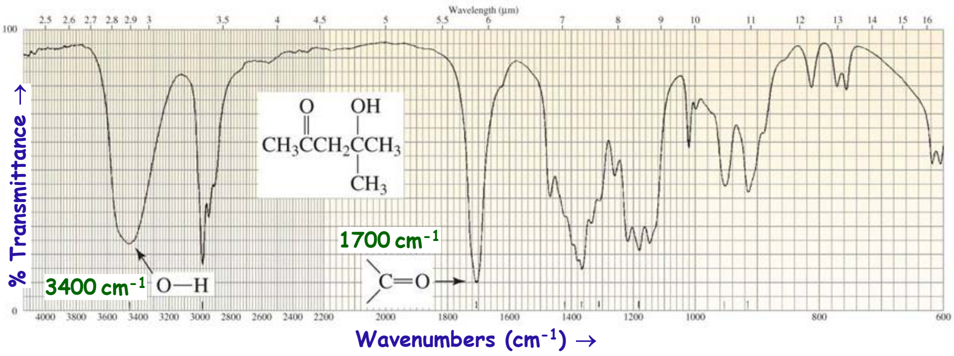
Modified from: http://www.chem.ucalgary.ca/groups/wieser/instru~1.GIF

**Optics & sample holder: must be ~transparent to IR**

- **Avoid covalent bonds…**
- **Use simple ionic compounds**
  - Glassy plates made of KBr, CsI, *etc.*
  - **Your sample** = neat liquid: mix a drop into "nujol" oil
    & place between pre-made plates

    solid: mix with KBr(s)
    & press to form thin plate

## An IR absorption spectrum

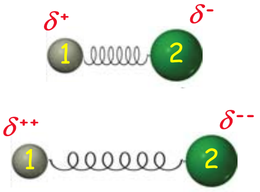


**Functional group region**
- characteristic absorptions
- reveals major functional groups
- very useful to synthetic chemists

**Fingerprint region**
- unique for each compound
- complex to analyze
- used by specialists…

Use tables of characteristic peak positions & intensities: Appendix VI

## 12.9 Intensities of Absorption Bands



**Vibrations cause dipole moment changes**

- $\mu$ = (magnitude of atom's $\delta$ charge) x ($d_{1-2}$)
- stretching ⇨ ↑$d_{1-2}$ ⇨ larger dipole moment

Greater change in dipole moment ⇨ more intense absorption
⇨ larger peak in spectrum

**Explains:**

**1. More polar bonds yield stronger absorbance**

- larger $|\delta^{+-}|$ ⇨ larger $\mu$ ⇨ higher intensity absorbance

O—H > N—H > C—H

Other trends:

**2. More bonds of given type ⇨ stronger absorbance**

**3. More concentrated sample ⇨ stronger absorbance**

## 12.8 Characteristic IR bands of functional groups

**Table 12.4**

| Type of bond | Wavenumber ($cm^{-1}$) | Intensity |
|---|---|---|
| C≡N | 2260–2220 | medium |
| C≡C | 2260–2100 | medium to weak |
| C=C | 1680–1600 | medium |
| C=N | 1650–1550 | medium |
|  | ~1600 and ~1500–1430 | strong to weak |
| C=O | 1780–1650 | strong |
| C—O | 1250–1050 | strong |
| C—N | 1230–1020 | medium |
| O—H (alcohol) | 3650–3200 | strong, broad |
| O—H (carboxylic acid) | 3300–2500 | strong, very broad |
| N—H | 3500–3300 | medium, broad |
| C—H | 3300–2700 | medium |

**Intensity descriptors:**
- s, m, w
- broad (br), sharp (sh)

**Broad peaks:**
- **hydrogen-bonding**

⇨ weakens X-H bond
⇨ sample's molecules won't have exactly same X-H strength
⇨ distribution of X-H stretching frequencies

*(Details: 12.12)*

**Higher frequency if:**
- stronger bond
- higher bond order

*(Details: 12.10)*

**Higher intensity if:**
- higher polarity bond
- more bonds of that type

*(Details: 12.9)*

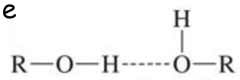
## Characteristic absorption bands

(12.11…2nd half)

**O-H bands & N-H bands:** intense, characteristic

- broadened if H-bonded: *e.g.,* concentrated sample

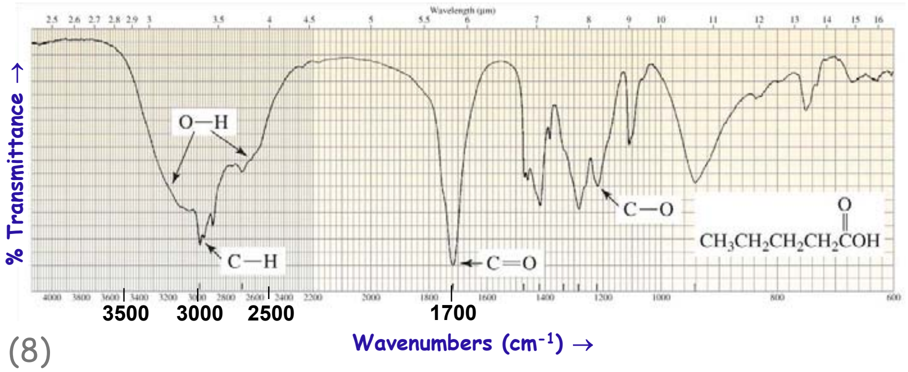
R—O—H
dilute solution
3650–3590 $cm^{-1}$



$$R{-}O{-}H\cdots\overset{\displaystyle H}{\overset{|}{O}}{-}R$$

concentrated solution
3550–3200 $cm^{-1}$

Fig.12.20 - **IR spectrum of pentanoic acid**



## C-H bands: yield information about hybridization of C…

- **C-H Stretches: reveal nature of hydrocarbon chain** **Table 12.5**

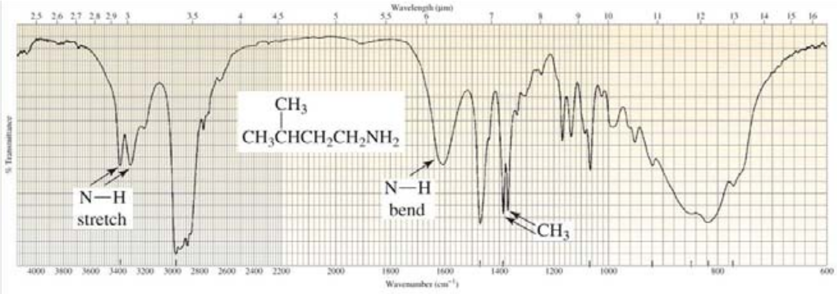
| | | | |
|---|---|---|---|
| $C\equiv C-H$ | ~3300 | $cm^{-1}$ | sp |
| $C=C-H$ | 3100–3020 | | $sp^2$ |
| $C-C-H$ | 2960–2850 | | $sp^3$ |
| $R-\overset{\overset{O}{\|}}{C}-H$ | ~2820 and ~2720 | | |

**higher s-character**
⇨ stronger bonds
⇨ higher $cm^{-1}$ stretch

**unique position (∴obvious…)**

- **C-H Bends: can reveal methyl groups**
  - if see $sp^3$ C-Hs: check just right of 1400 $cm^{-1}$ ⇨ $CH_3$ bend

(9)



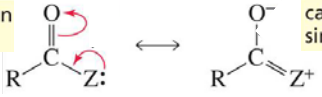
## 12.11 Relative positions of Absorption Bands

### ⇨ tells about: EDGs, EWGs, delocalization, H-bonding…

**Resonance effects: Electron delocalization**

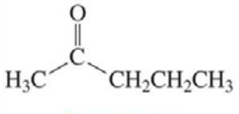
- can change bond strength - *i.e.,* average bond order
- look for other resonance structures – case-by-case…
  - **including bond/no-bond structures**

resonance electron donation



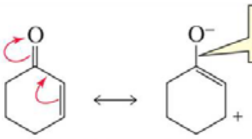
carbonyl group has some single-bond character

Fig.12.15-16: Isolated ketone *vs.* Conjugated ene-one



**2-pentanone**

$C=O$ at 1720$cm^{-1}$



carbonyl group has some single-bond character

**2-cyclohexenone**

$C=O$ at 1680$cm^{-1}$

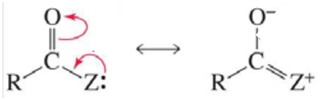
*Weaker bond ⇨*
*IR band at lower $cm^{-1}$*

## 12.11 Relative positions of Absorption Bands

⇨ tells about: EDGs, EWGs, delocalization, H-bonding…

**Inductive effects: Adjacent EDGs or EWGs**

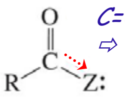
- Heteroatoms with lone pairs
  - 2 possibilities: Resonance e$^-$ donation *vs.* Inductive e$^-$ withdrawal



resonance electron donation

*Weakens C=O*
*⇨ band at lower cm$^{-1}$*

***vs.***



*C=O actually "tightened"*
*⇨ band at higher cm$^{-1}$*

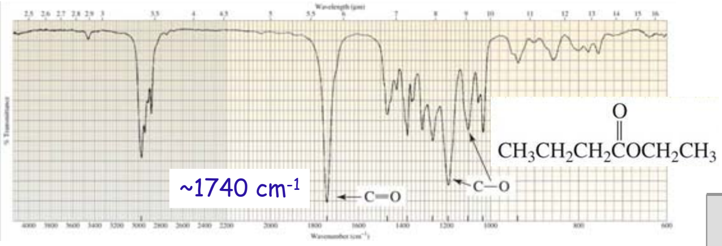
inductive electron withdrawal

**Which effect dominates?**

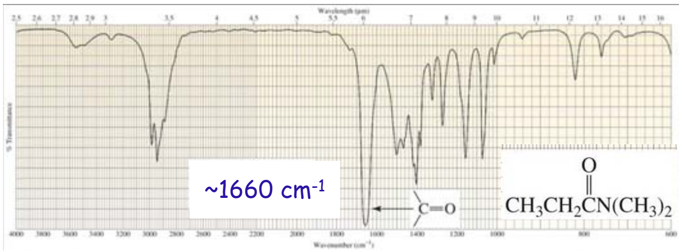
- look at typical absorption band positions…

**Esters:** O acts predominantly as inductive EWG
***vs.* Amides:** N acts predominantly as resonance EDG

Rationalize - draw resonance structures



~1740 cm$^{-1}$



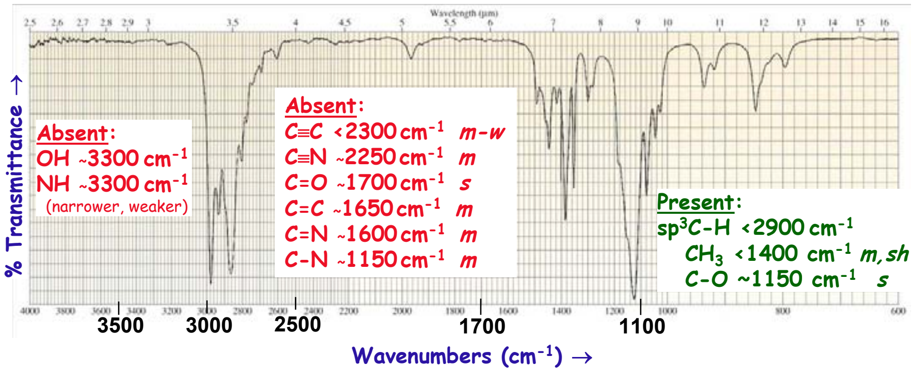
~1660 cm$^{-1}$

| **C=O stretches** (average…) | |
|---|---|
| | **cm$^{-1}$** |
| amide | 1660 |
| ketone<br>aldehyde | 1720 |
| acid | 1720 |
| ester | 1740 |

Fig.12.17-18

## 12.13,15 **Interpretting IR spectra: what is & isn't there?**

1. **Look for key absorptions:** identify & rule out functional groups.
2. **Do not expect to solve a structure using only an IR spectrum.**
    - Combine IR data with other evidence.
    - BUT: final structure must be consistent with IR data.



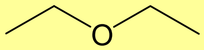
**Absent:**
OH ~3300 $cm^{-1}$
NH ~3300 $cm^{-1}$
(narrower, weaker)

**Absent:**
C≡C <2300 $cm^{-1}$ *m-w*
C≡N ~2250 $cm^{-1}$ *m*
C=O ~1700 $cm^{-1}$ *s*
C=C ~1650 $cm^{-1}$ *m*
C=N ~1600 $cm^{-1}$ *m*
C-N ~1150 $cm^{-1}$ *m*

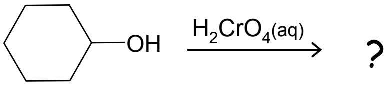
**Present:**
$sp^3$C-H <2900 $cm^{-1}$
$CH_3$ <1400 $cm^{-1}$ *m, sh*
C-O ~1150 $cm^{-1}$ *s*

**= An ether**
with methyl groups (not THF…)

Ans:



## **Have you isolated your desired product?**



**TLC of rxn mixture:** 2 main components

↓

**DISTILLATION:** 2 colourless liquids, pure (verified by TLC)

Analyses of **one** of them…

**UV spectrum:** of neat liquid -- no bands 200-320 nm

**IR spectrum:**
of thin film
of liquid
between
KBr plates

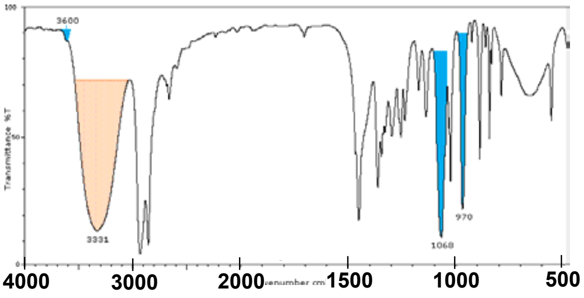
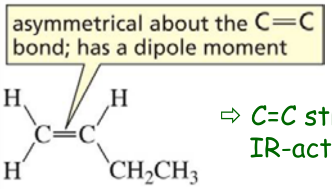


Image from: http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/irspec1.htm

## 12.14 Some vibrations are IR-inactive

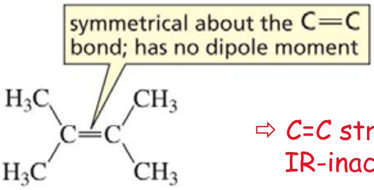
**If bond has no dipole moment…**

- its vibrations won't to a change ⇨ won't absorb IR radiation


asymmetrical about the C=C bond; has a dipole moment

**1-butene**

⇨ C=C stretch
IR-active


symmetrical about the C=C bond; has no dipole moment

**2,3-dimethyl-2-butene**

⇨ C=C stretch
IR-inactive

*Do these have any IR-inactive vibrations?*