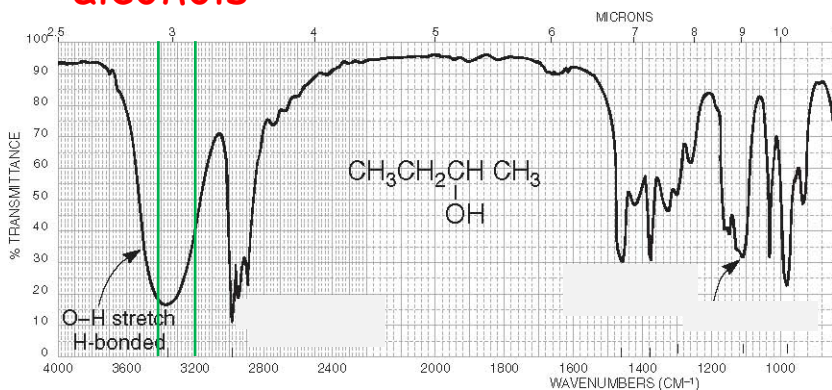


8. Spectrum continued

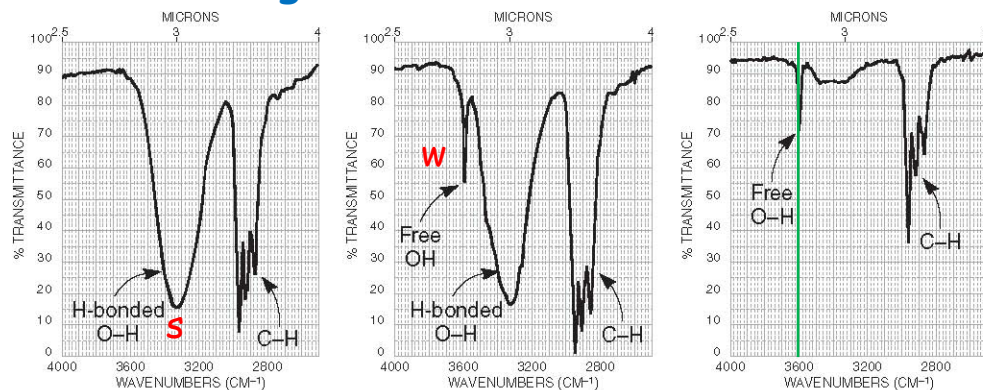
I. The $\nu(X-H)$ region

alcohols



3400-3200 $\nu(O-H)$

H-bonding in alcohols

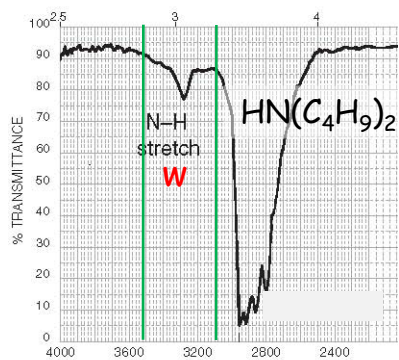


neat

increasing dilution

3600 free $\nu(O-H)$

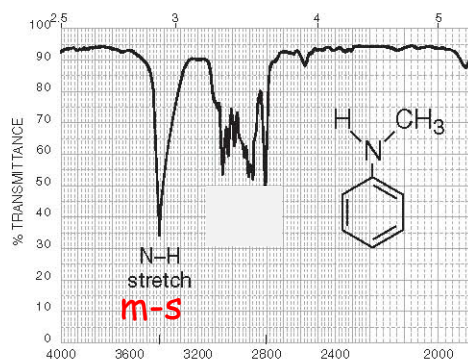
amines



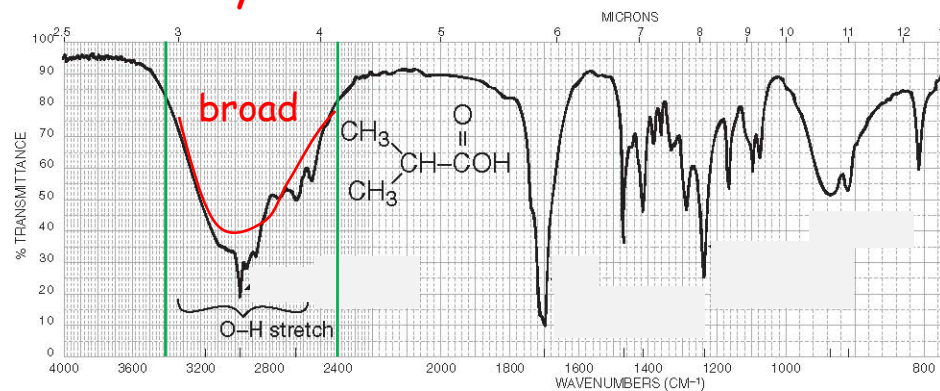
3500-3100 $\nu(N-H)$ -NH-

remember:

s and as for $-NH_2$



carboxylic acids



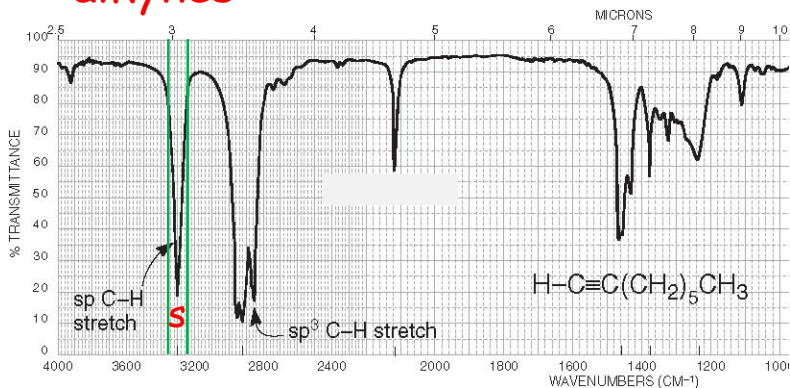
3400-2400 $\nu(O-H)$

-COOH

8. Spectrum continued

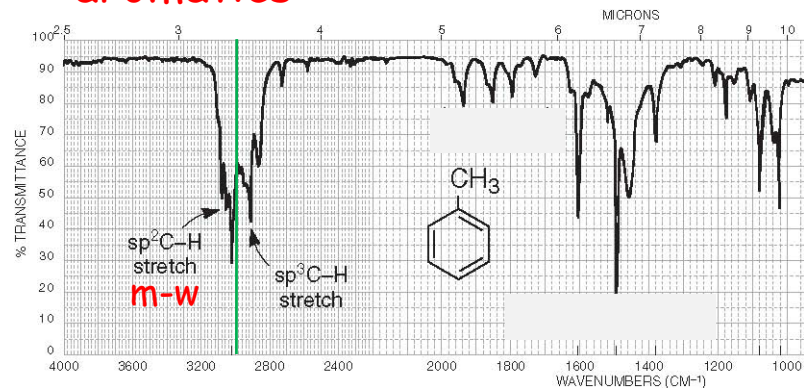
I. The $\nu(X-H)$ region

alkynes



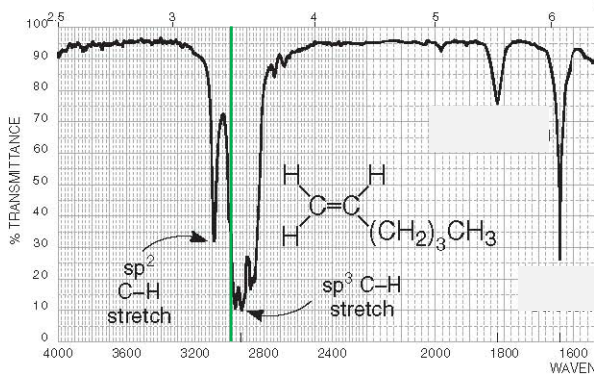
3300 $\nu(C-H)$ sp

aromatics



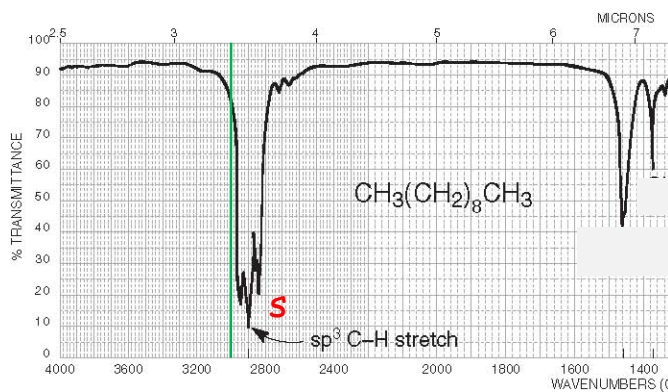
> 3000 $\nu(C-H)$ sp²

alkenes



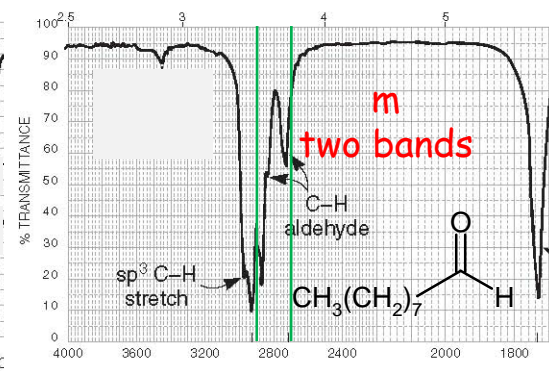
> 3000 $\nu(C-H)$ sp²

alkanes



< 3000 $\nu(C-H)$ sp³

aldehydes



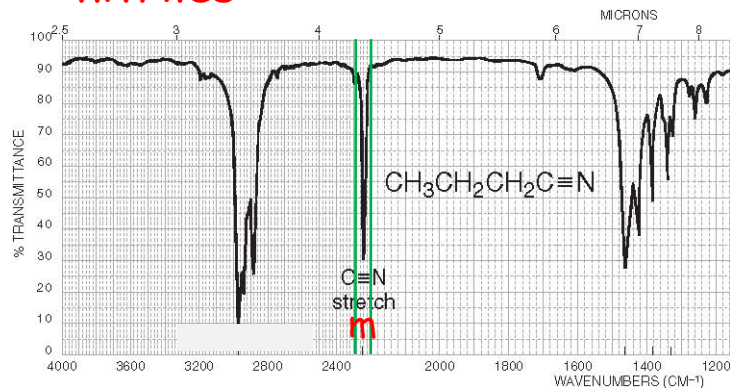
2900-2700 $\nu(C-H)$ sp²

-CHO

8. Spectrum continued

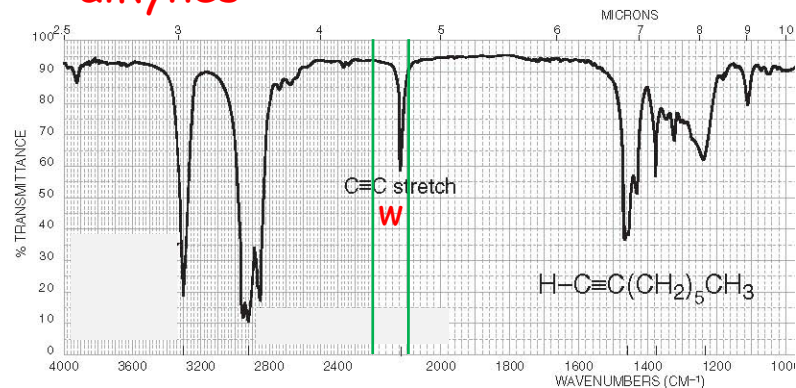
II. The $\nu(X\equiv X)$ region

nitriles



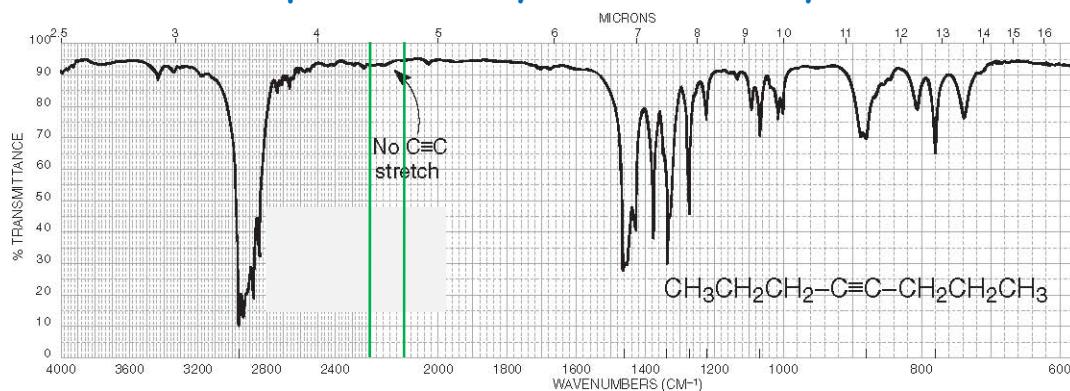
2300-2200 $\nu(\text{C}\equiv\text{N})$

alkynes



2250-2100 $\nu(\text{C}\equiv\text{C})$

...but compare the symmetric alkyne

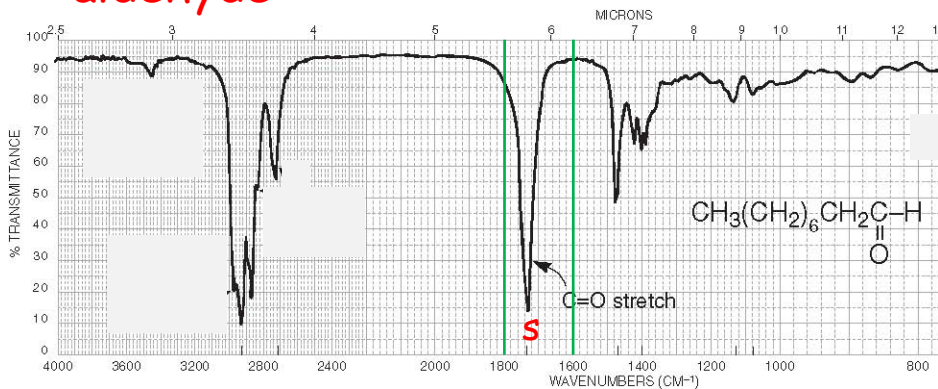


...the same would be true for $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_2\text{CH}_2\text{CH}_3$
pseudo-symmetric

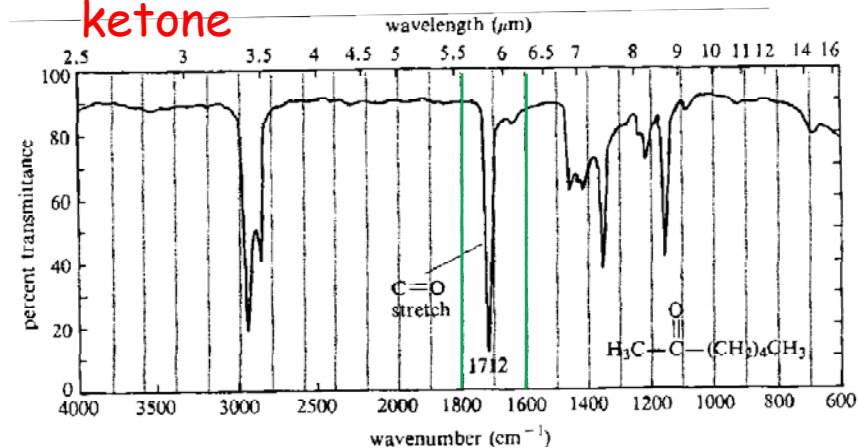
8. Spectrum continued

III. The $\nu(\text{C}=\text{O})$ region: 1800-1600 cm^{-1}

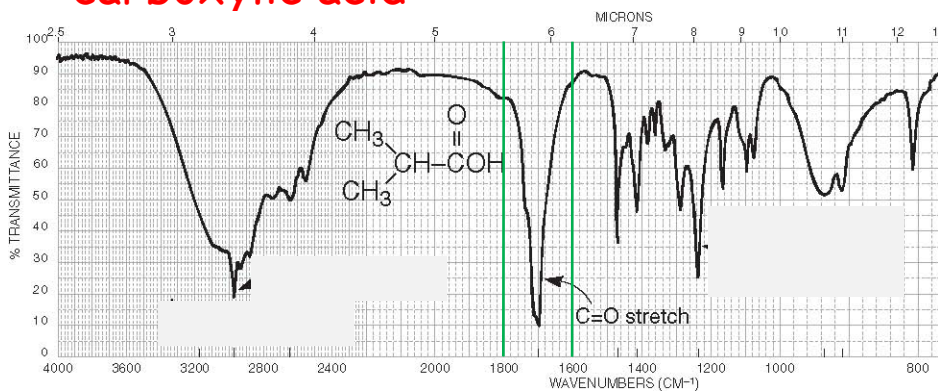
aldehyde



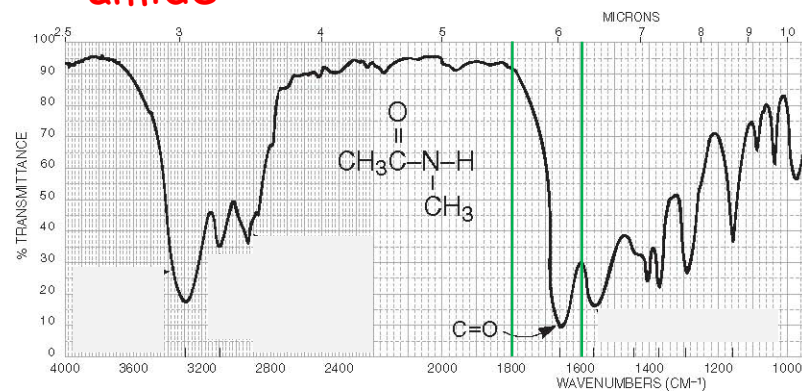
ketone



carboxylic acid



amide



further assignment

through the exact position

in the 1800-1600 cm^{-1} window:

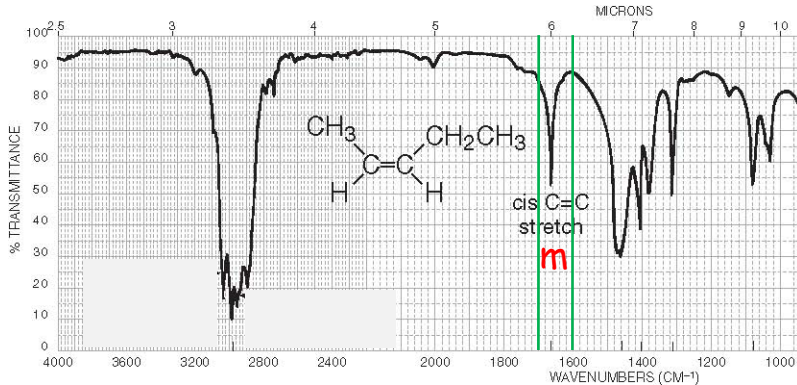
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide

← cm^{-1} →

8. Spectrum continued

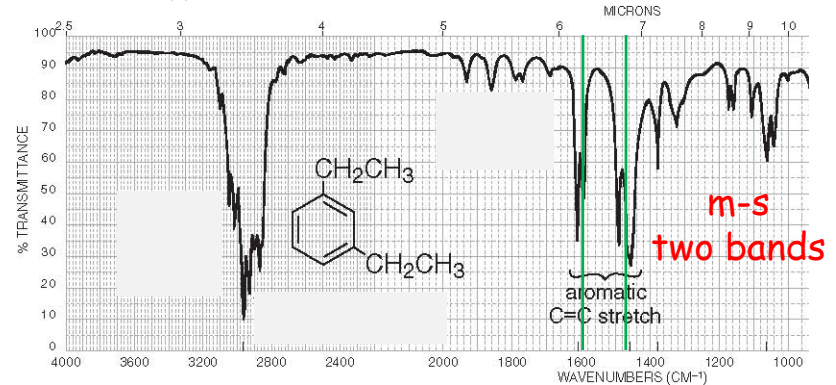
IV. The $\nu(\text{C}=\text{C})$ region

alkenes



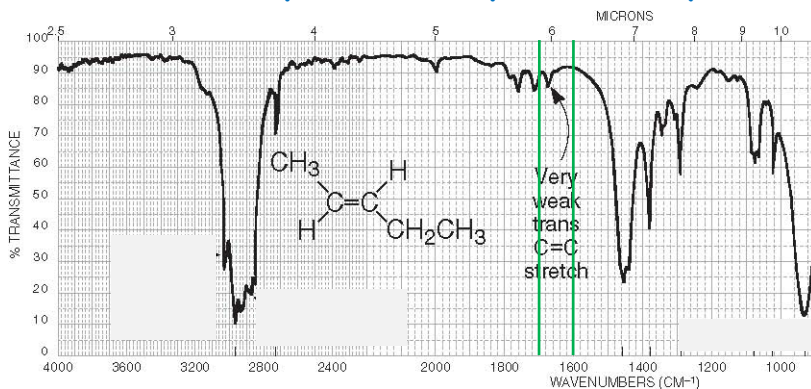
1700-1600 $\nu(\text{C}=\text{C})$

aromatics



1600 and 1475 $\nu(\text{C}=\text{C})$
aromatic

...but compare the pseudo-symmetric alkene



1700-1600 $\nu(\text{C}=\text{C})$

this is getting close to the fingerprint region: this is where our stretch analyses stop, even though some occur at smaller $\bar{\nu}$

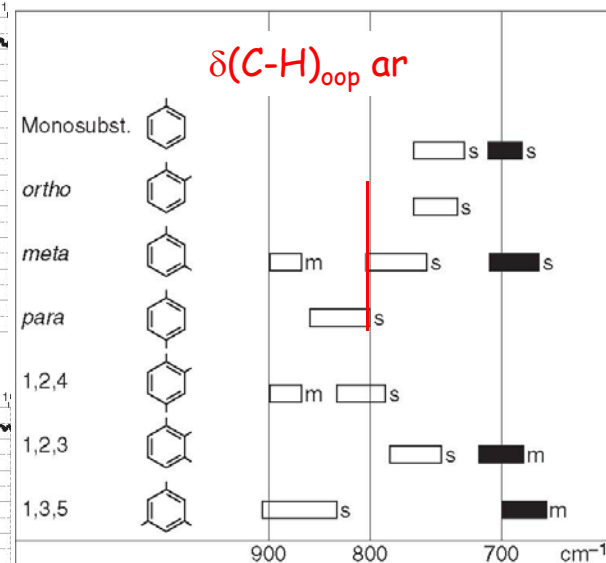
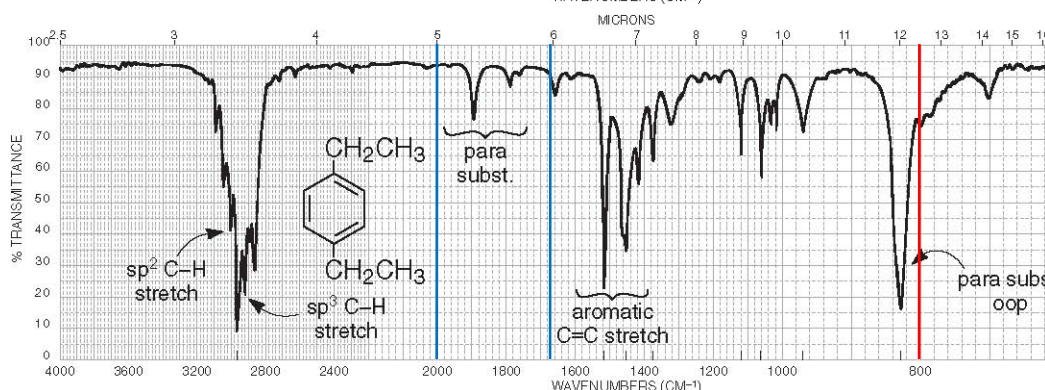
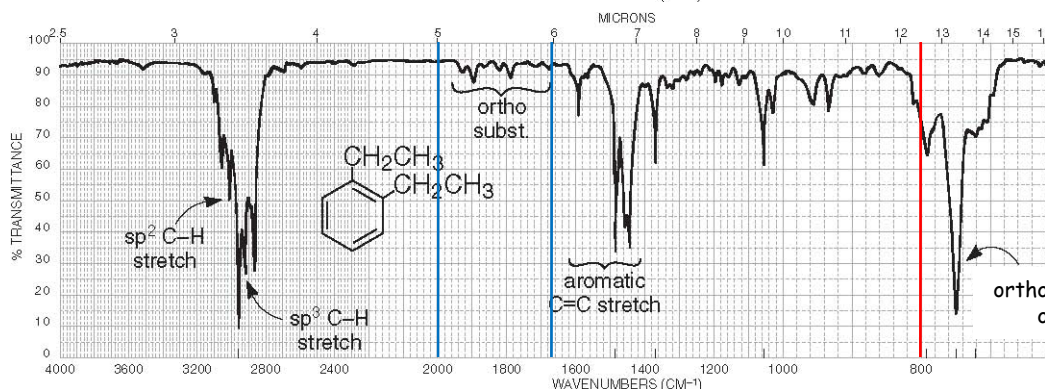
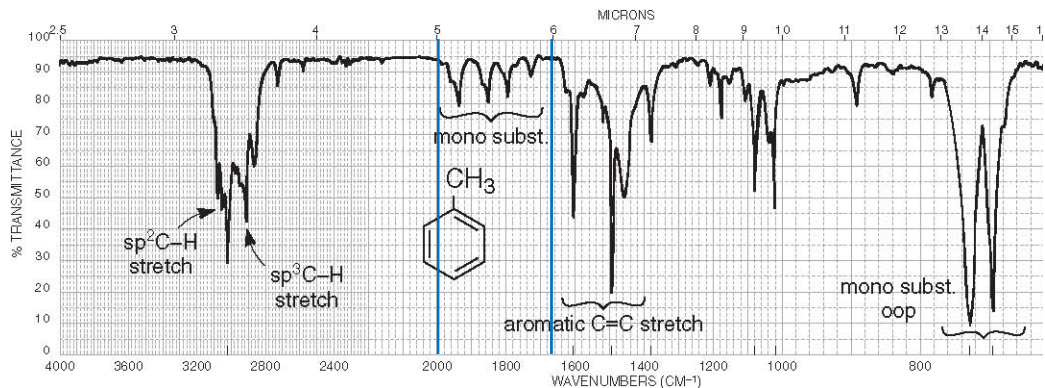
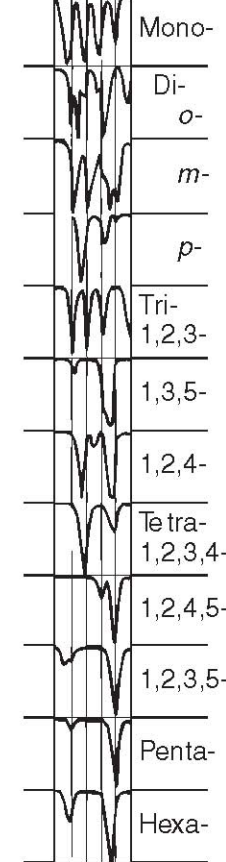
Ester C-O???

8. Spectrum continued

V. Substitution patterns on an aromatic ring

overtone
and
combination

2000 1667 cm^{-1}

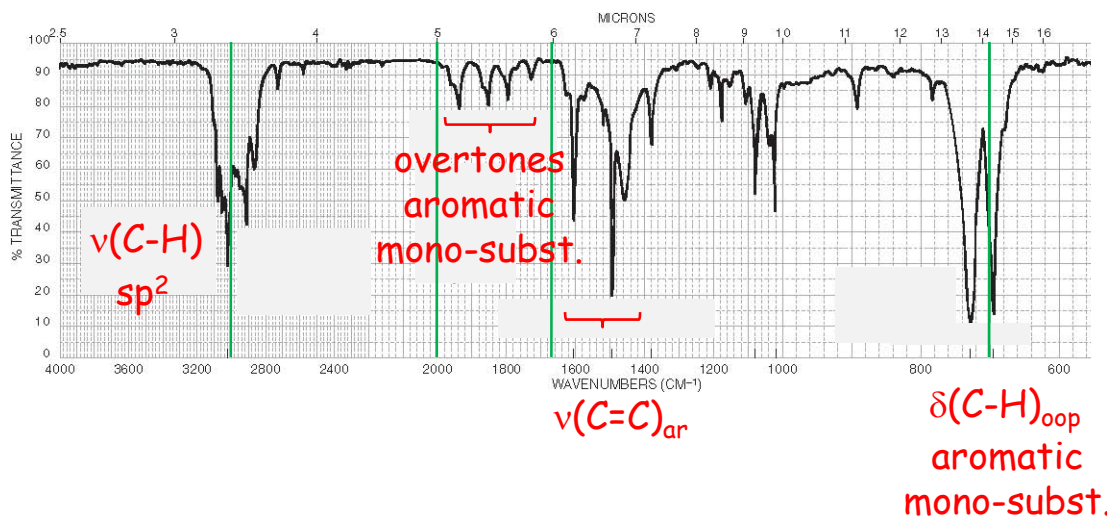


give one of these labels
as a qualifier on
 $\delta(\text{C-H})_{\text{oop ar}}$

8. Spectrum continued

V. Substitution patterns on an aromatic ring

- how to refine information gained upon $\nu(\text{C-H})_{\text{sp}^2}$ for an aromatic system

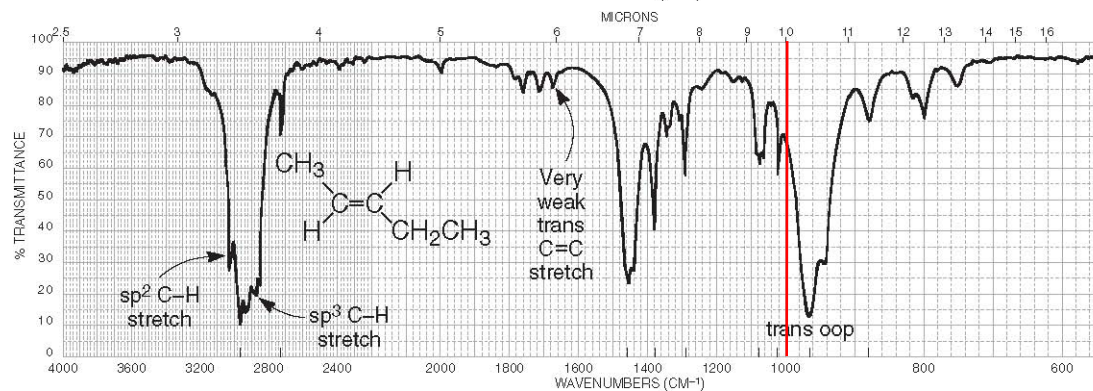
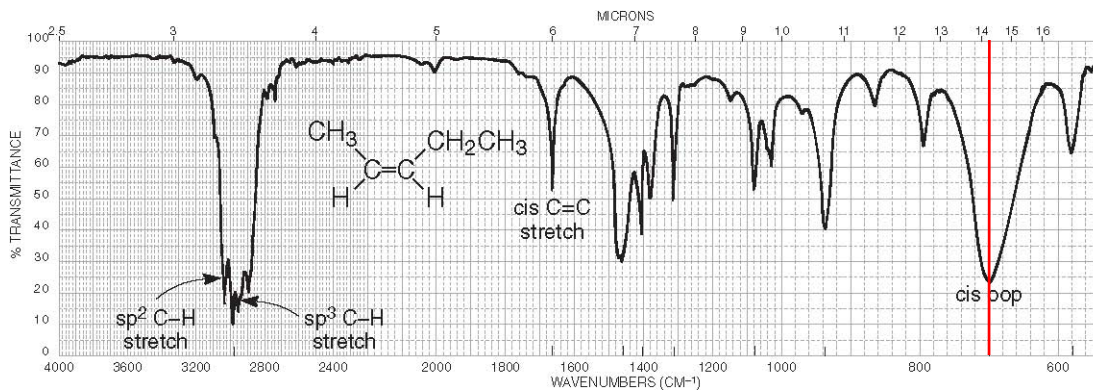
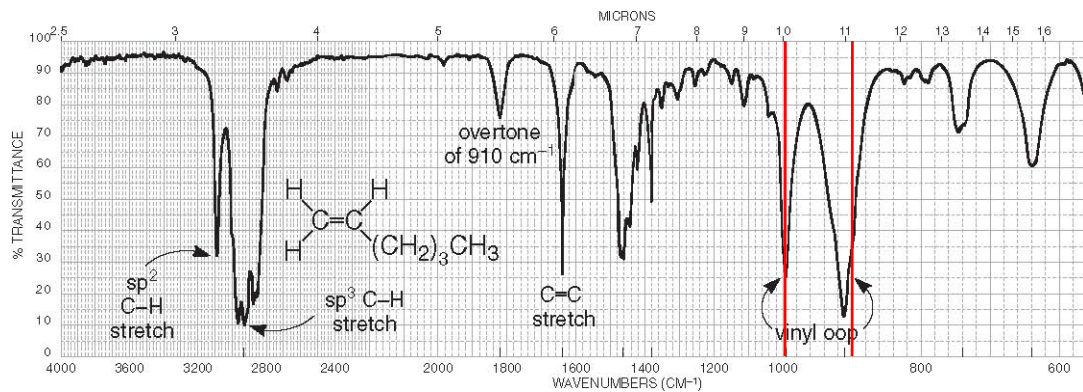
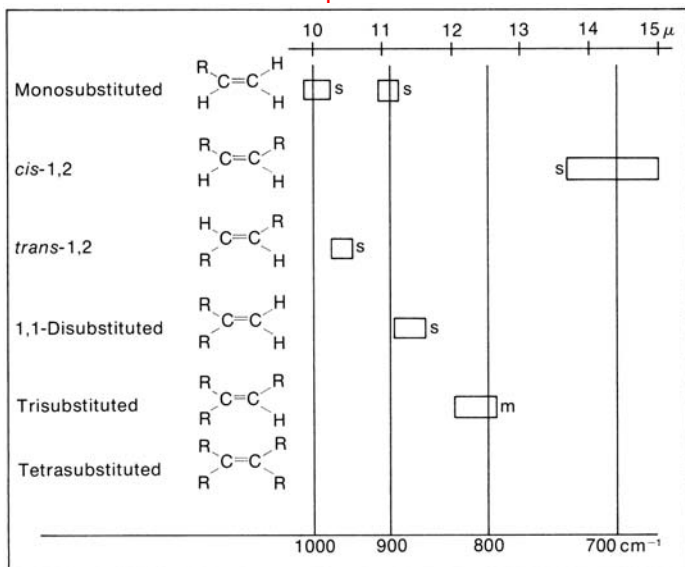


- check around 3000 cm^{-1} : $> 3000 \nu(\text{C-H})_{\text{sp}^2}$
- check the $\nu(\text{C}=\text{C})$ region: pattern suggests $\nu(\text{C}=\text{C})_{\text{ar}}$
- check between 2000 and 1670 cm^{-1} : overtones are present, pattern suggests aromatic mono-substitution
- check in the fingerprint between 900 and 690 cm^{-1} : two bands present, $\delta(\text{C-H})_{\text{oop}}$, pattern suggests aromatic mono-substitution

8. Spectrum continued

VI. Substitution patterns on an alkene C=C

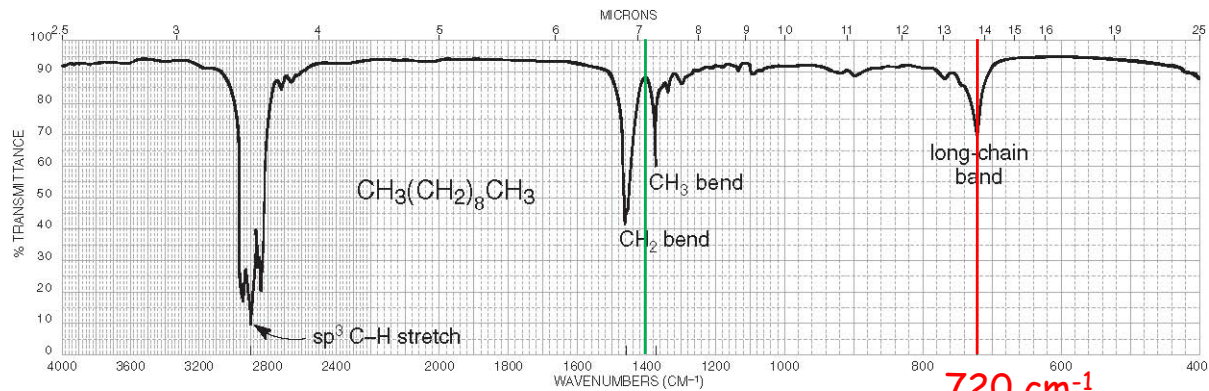
$\delta(C-H)_{oop}$ alkene



give one of these labels as a qualifier on $\delta(C-H)_{oop}$ alkene

8. Spectrum continued

VII. Deformation bands from CH₂ and CH₃ groups

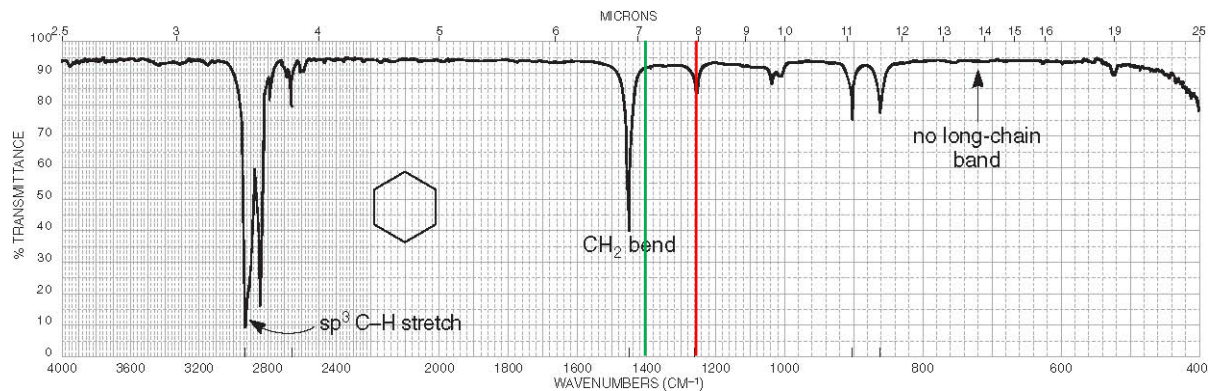
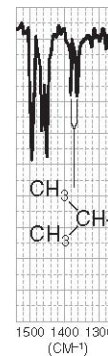


> 1400 δ(CH₂)
scissoring

< 1400 δ(CH₃)

720 cm⁻¹
δ(CH₂)
rocking

δ(CH₃)
patterns for
iso-propyl tert-butyl



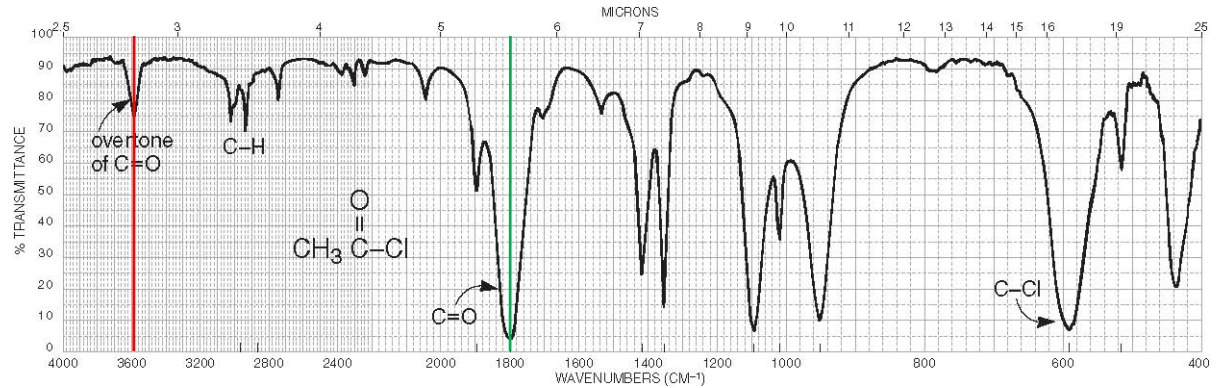
1250 δ(CH₂)
wagging, twisting

} w, don't need to identify

8. Spectrum continued

VIII. More overtones

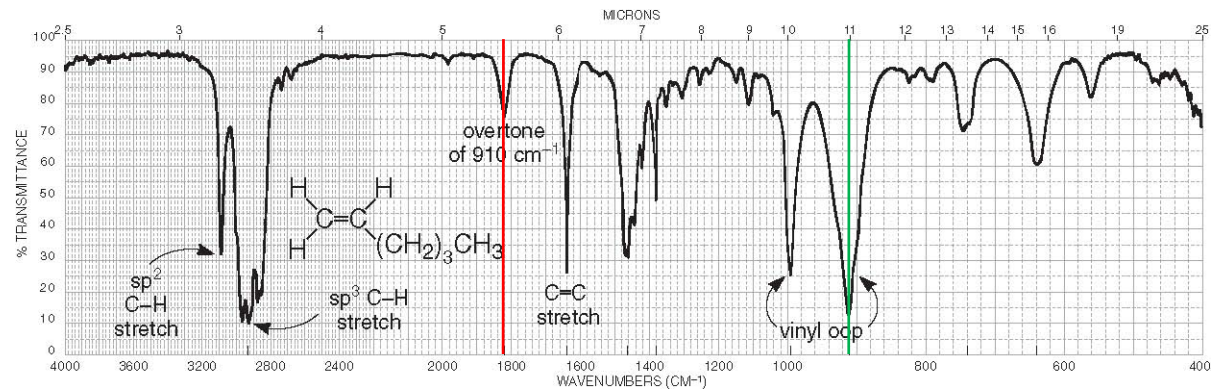
very common:



3600 = 2 · 1800
overtone,
not ν(N-H)!

1800 ν(C=O)

also common:

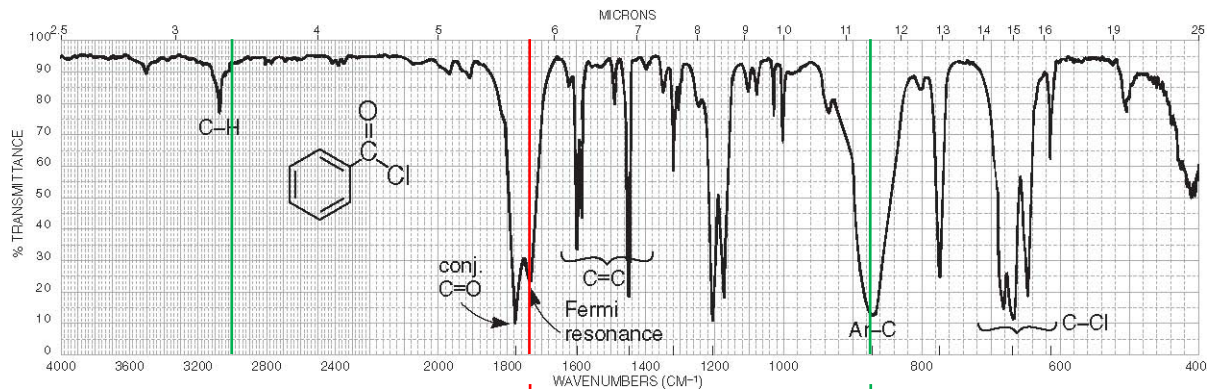


1820 = 2 · 910
overtone,
not ν(C=O)!

910 δ(C-H)_{oop} alkene

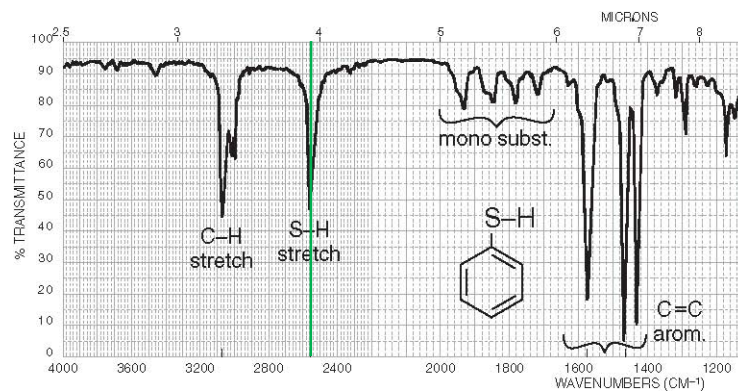
8. Spectrum continued

IX. Various additional information



> 3000 $\nu(\text{C-H})$ sp^2
w, but important } need to identify

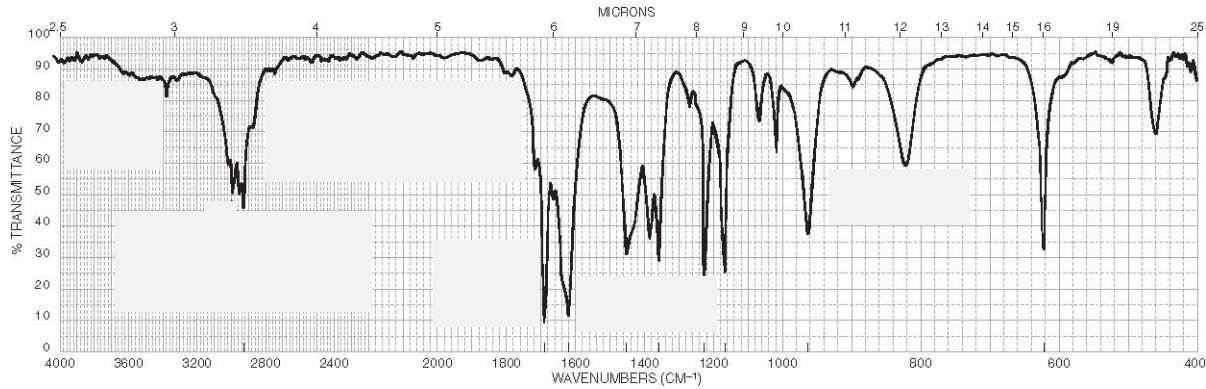
1740 = 2 · 870
overtone,
and $\nu(\text{C=O})$ at 1740:
Fermi-resonance band,
not a second $\nu(\text{C=O})$!



2550 $\nu(\text{S-H})$
not $\nu(\text{C}\equiv\text{C})$ or $\nu(\text{C}\equiv\text{N})$

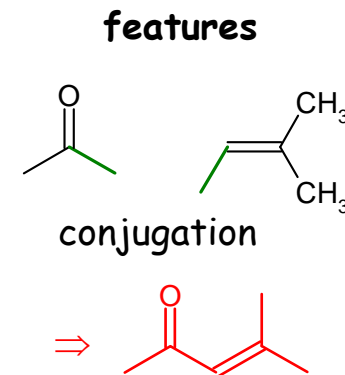
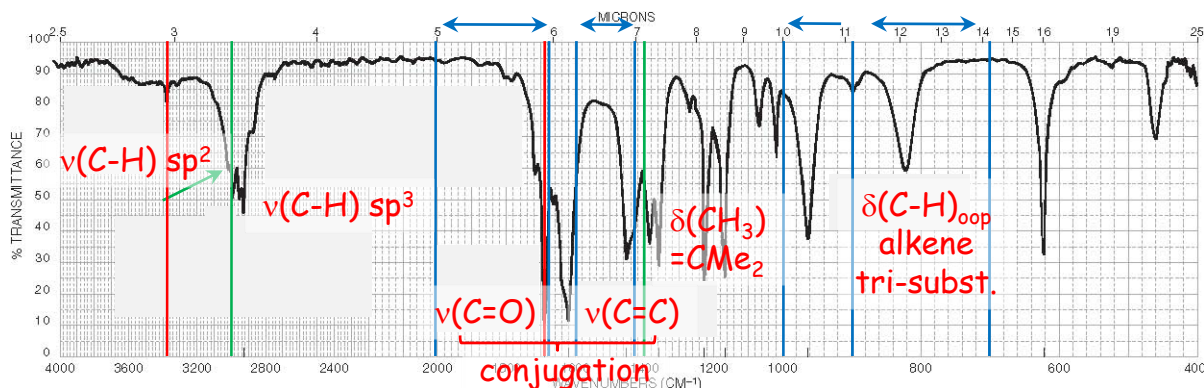
Example

A detailed analysis of an IR spectrum *without* any further information.



Example

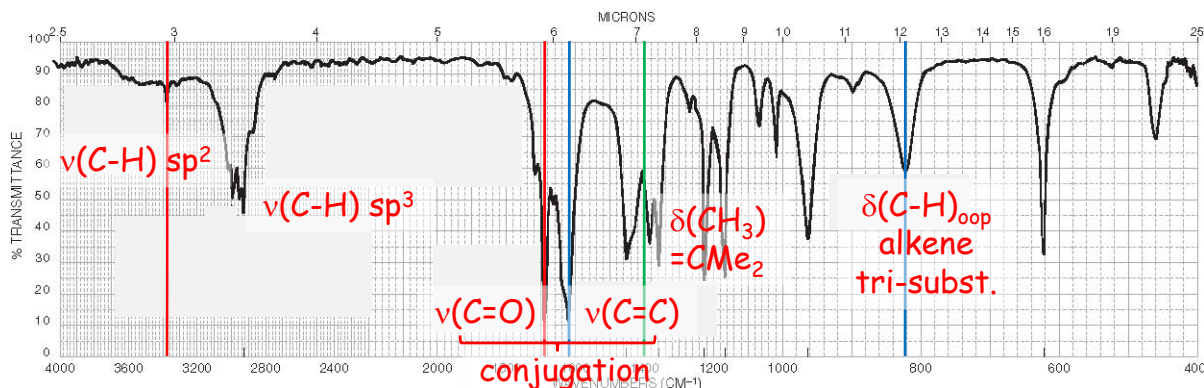
A detailed analysis of an IR spectrum *without* any further information.



- definitely: < 3000 $\nu(\text{C-H})$ sp^3
 - nothing directly > 1400, no $\delta(\text{CH}_2)$
 - < 1400 $\delta(\text{CH}_3)$, maybe some i-pr or t-bu-like pattern (p. 38)
- probably: > 3000 $\nu(\text{C-H})$ sp^2 ⇒ aromatic or alkene
- but:
 - below 2000 no aromatic overtones (p. 46)
 - around 1500 not the typical set of $\nu(\text{C=C})$ ar (p. 43)
 - 900-700 not s $\delta(\text{C-H})_{\text{oop}}$ aromatic para-subst. (p. 46) ⇒ probably not aromatic
 - > 1600 no typical $\nu(\text{C=C})$ alkene (p. 34), but lowered to 1620?
 - 1000-700 m $\delta(\text{C-H})_{\text{oop}}$ alkene tri-subst. (p. 42) ⇒ probably alkene, but not "typical"
- 3380 overtone of $\nu(\text{C=O})$ at $3380/2 = 1690$ ⇒ very low, in amide region ⇒ or again not "typical"
- $\nu(\text{C=O})$ not aldehyde, not acid, not ester, not amide ⇒ probably ketone (not "typical")
- lowered $\nu(\text{C=C})$ alkene and lowered $\nu(\text{C=O})$ ketone point to conjugation

Example continued

A detailed analysis of an IR spectrum *with* further information.



- elemental analysis gives $\text{C}_6\text{H}_{10}\text{O}$
- $U = 6 + 1 - \frac{1}{2}(10 - 0) = 7 - 5 = 2$
- possibly $\text{C}=\text{O}$ and $\text{C}=\text{C}$ alkene or ring
- check for alkene substitution pattern: 5 C taken care of
- check for aldehyde or ketone: 6th C taken care of, plus O, plus all H
- notice the possible conjugation, check whether those bands fit
- notice the absence of CH_2 , check whether those bands are absent
- check whether everything makes sense (small $\nu(\text{C-H}) \text{ sp}^2$...)
- put all appropriate labels

