

Nuclear Magnetic Resonance Spectroscopy Depends on Nuclear Spin

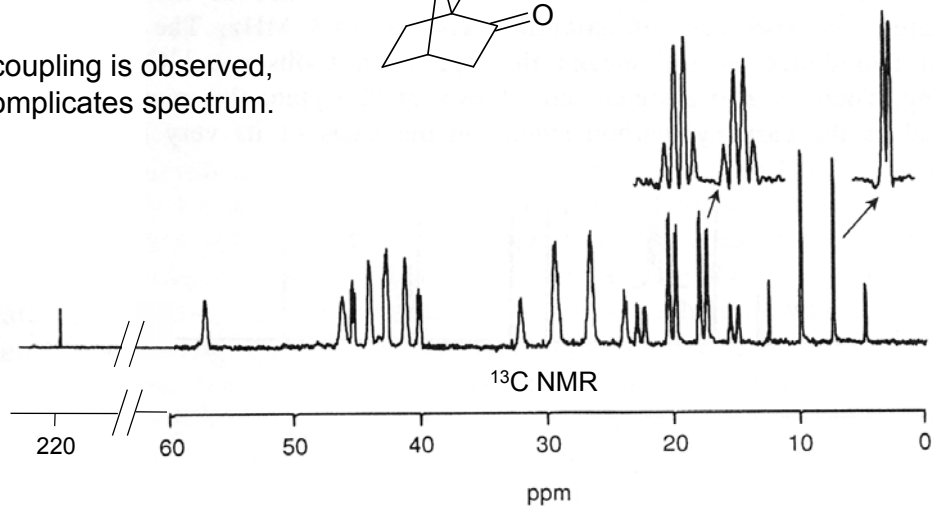
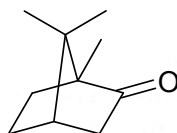
<u>Nucleus</u>	<u>Spins</u>	<u>Isotope Abundance</u>
^1H	$\pm\frac{1}{2}$	99.9%
^{12}C	0	98.9%
^{13}C	$\pm\frac{1}{2}$	1.1%
^{19}F	$\pm\frac{1}{2}$	100%
^{31}P	$\pm\frac{1}{2}$	100%

^{13}C NMR measures only a small fraction of naturally occurring carbon.

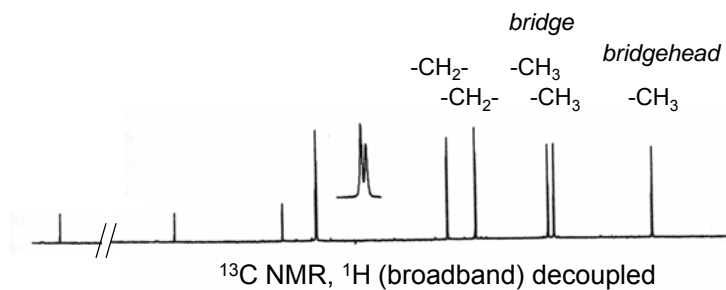
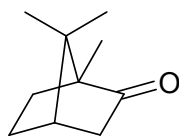
^{13}C NMR: A Problem With Coupling

$^1\text{H}\leftarrow\text{C}$ coupling not observed;
abundance of ^{13}C too low.

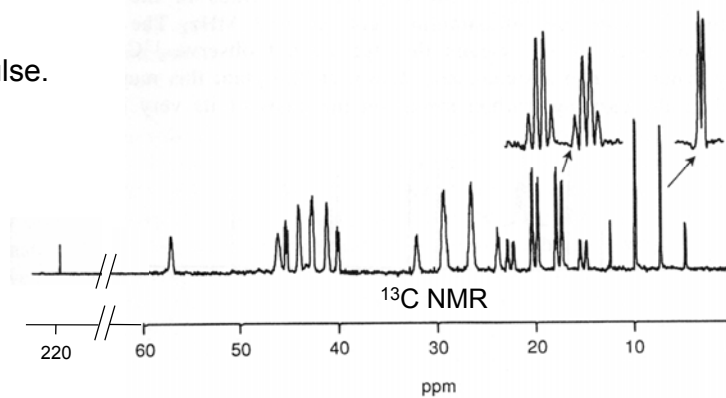
$^{13}\text{C}\leftarrow\text{H}$ coupling is observed,
and complicates spectrum.



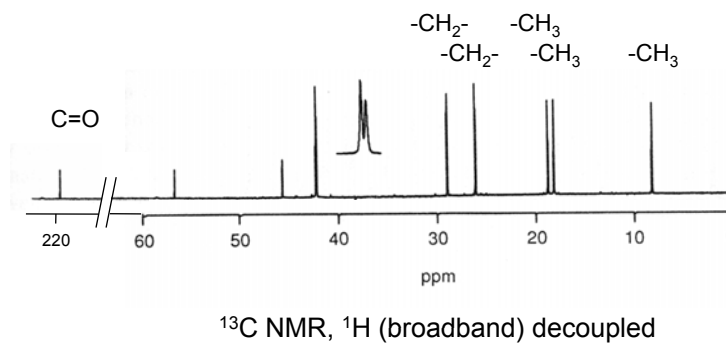
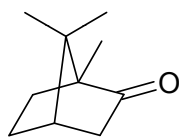
^1H -Decoupled ^{13}C NMR



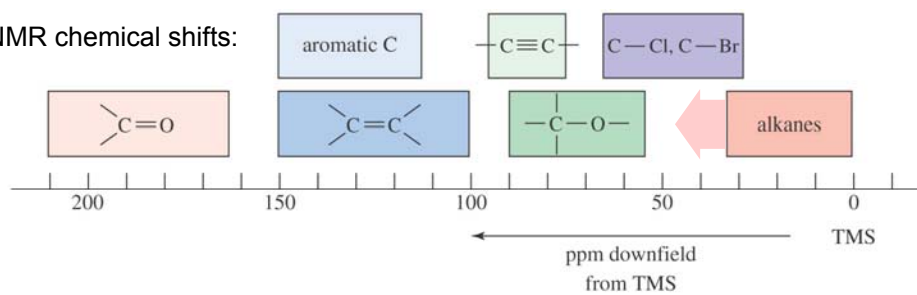
Solution: Decoupling pulse.



^1H -Decoupled ^{13}C NMR

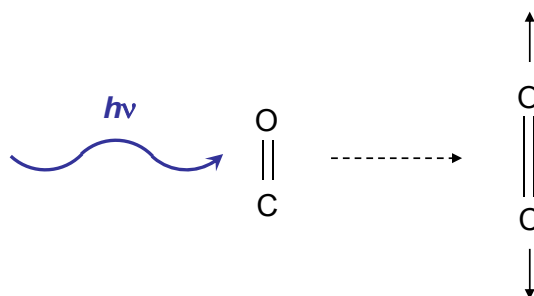


Typical ^{13}C NMR chemical shifts:

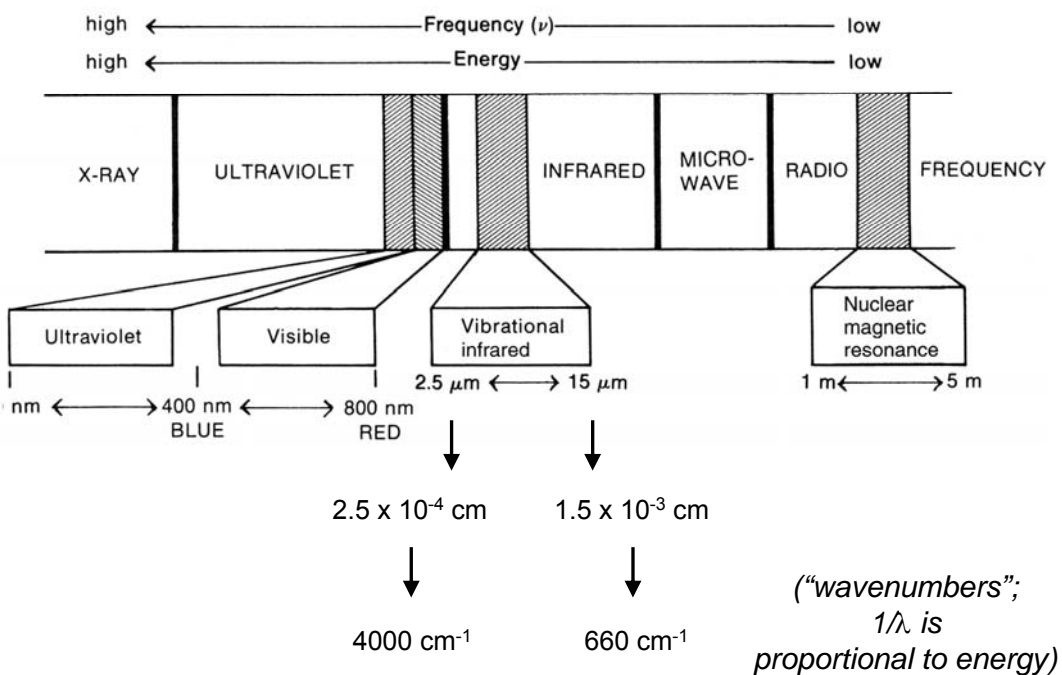


Infrared (IR) Spectroscopy

- Used to identify specific functional groups
- No information on total structure, connectivity
- Measures absorption of light by vibrational modes of specific bonds (and combinations of bonds)



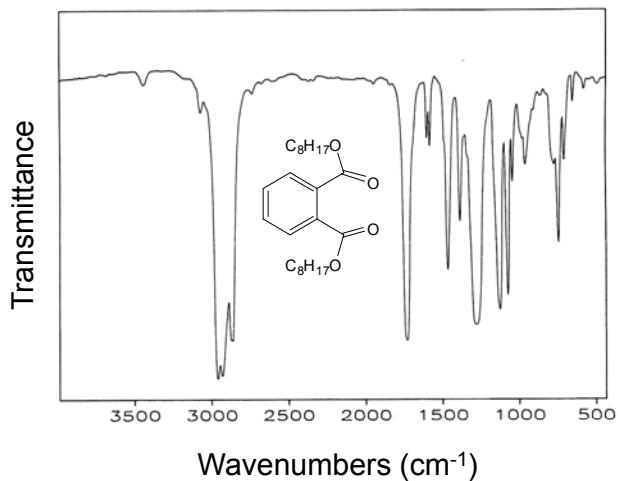
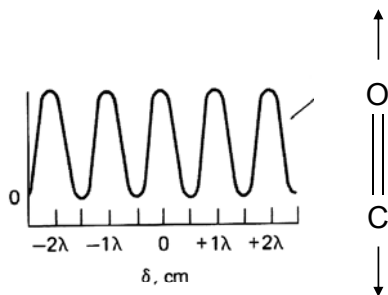
IR Spectroscopy



IR Spectroscopy: Methods

Instrument varies wavelength of light to match vibrational frequency of bonds.

Molecules are mostly transparent to IR light, but when frequency matches a bond vibration, light doesn't pass through.

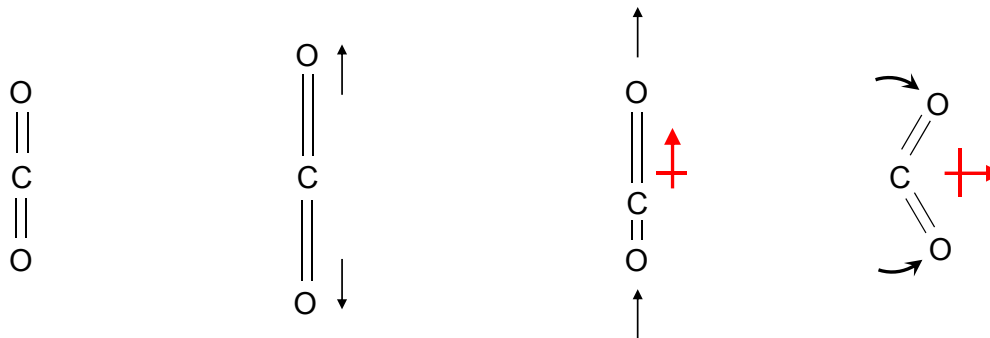


Okay, I lied. Modern instruments excite all wavelengths at once, deconvolute with Fourier transform.

IR Spectroscopy: Quantum Limitations

IR-absorbing transitions are allowed only when dipole moment changes during vibrational motion.

Modes can be combinations of bond vibrations. (Modes mix.)



symmetric stretch:
IR forbidden
(1340 cm^{-1})

asymmetric stretch:
IR allowed
(2350 cm^{-1})

bend:
IR allowed
(660 cm^{-1})

As a result, IR instruments sometimes purged with N_2 to get rid of CO_2 .

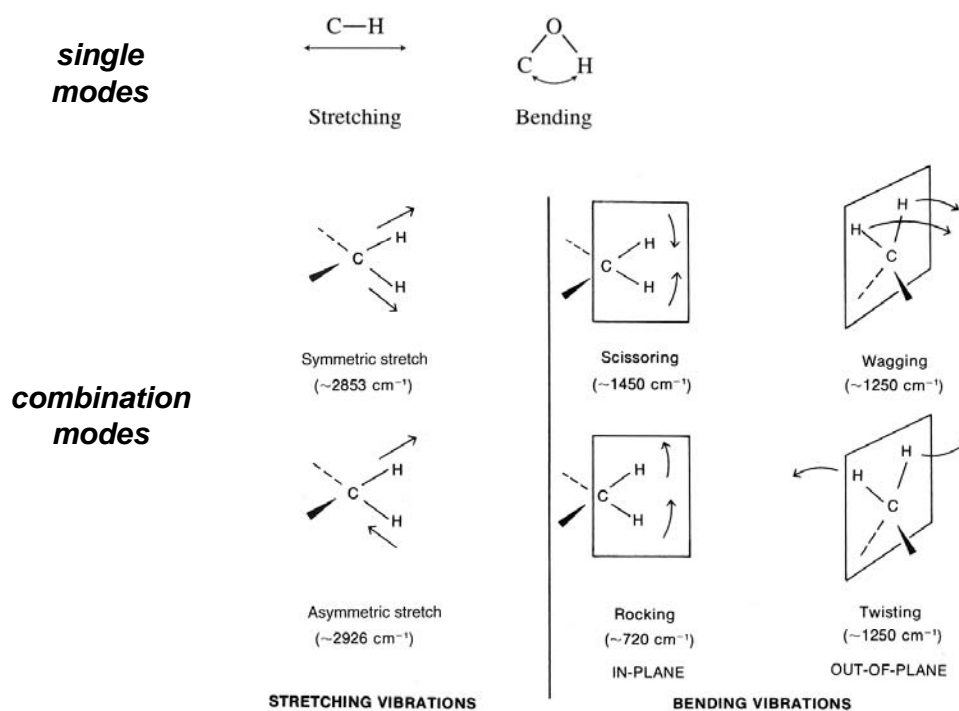
TABLE 12-2 Summary of IR Stretching Frequencies

Frequency (cm ⁻¹)	Functional Group	Comments	
3300	alcohol amine, amide alkyne	O—H N—H ≡C—H	always broad may be broad, sharp, or broad with spikes always sharp, usually strong
3000	alkane		just below 3000 cm ⁻¹
	alkene		just above 3000 cm ⁻¹
	acid	O—H	very broad
2200	alkyne nitrile	—C≡C— —C≡N	just below 2200 cm ⁻¹ just above 2200 cm ⁻¹
1710 (very strong)	carbonyl		ketones, aldehydes, acids esters higher, about 1735 cm ⁻¹ conjugation lowers frequency amides lower, about 1650 cm ⁻¹
1660	alkene		conjugation lowers frequency aromatic C=C about 1600 cm ⁻¹
	imine		stronger than C=C
	amide		stronger than C=C (see above)

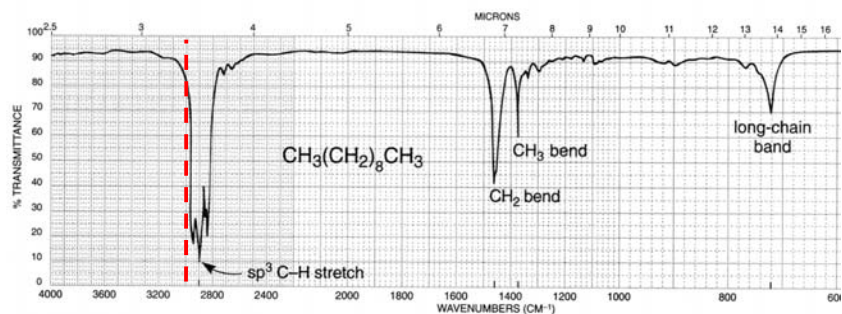
Ethers, esters, and alcohols also show C—O stretching between 1000 and 1200 cm⁻¹.

Much more than NMR, IR is used by matching spectrum peaks to a table.

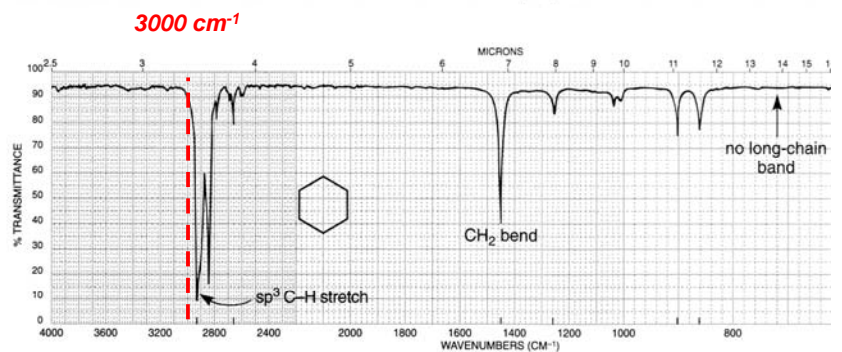
IR-Allowed C-H Vibrations



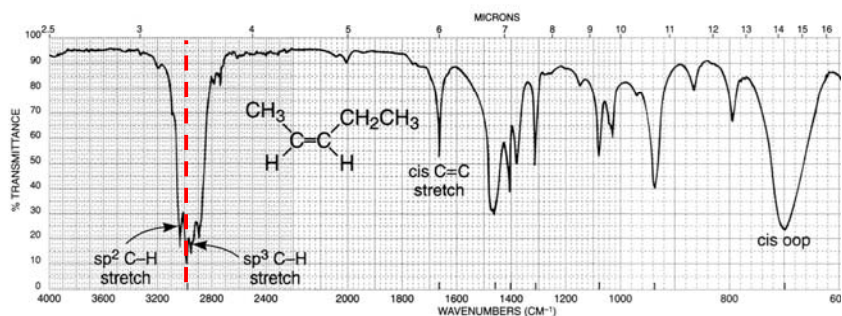
Characteristic Features in IR: Alkanes



C-H stretch **below** 3000 cm^{-1} .

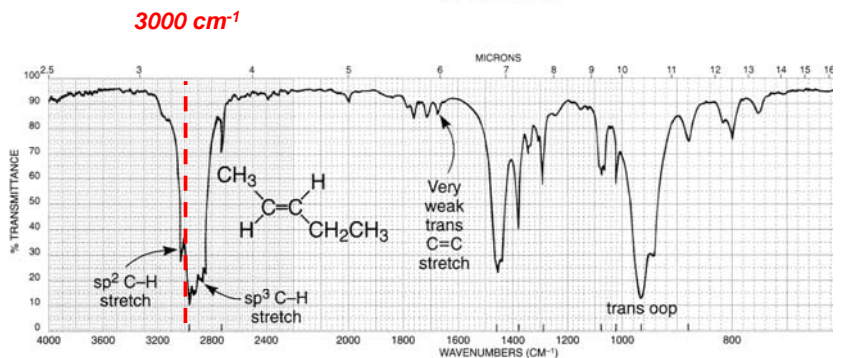


Characteristic Features in IR: Alkenes



C-H stretch **above** 3000 cm^{-1} .

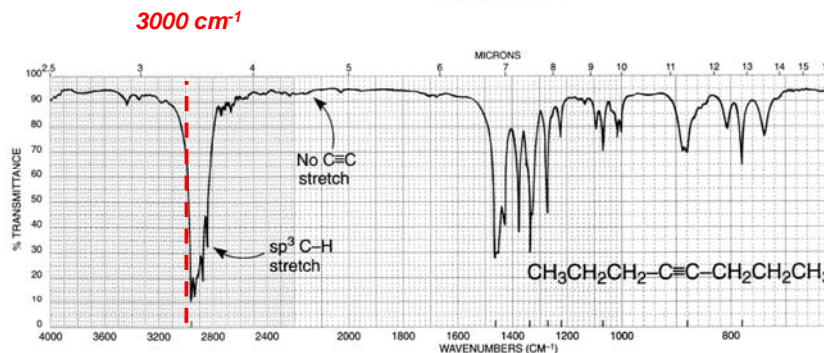
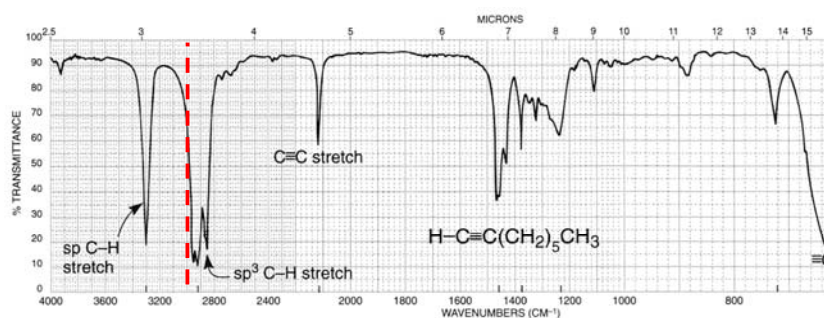
C=C stretch
 $\sim 1600\text{-}1660 \text{ cm}^{-1}$;
 affected by bond
 stereochemistry.



Characteristic Features in IR: Alkynes

C-H stretch
~ 3300 cm^{-1} .

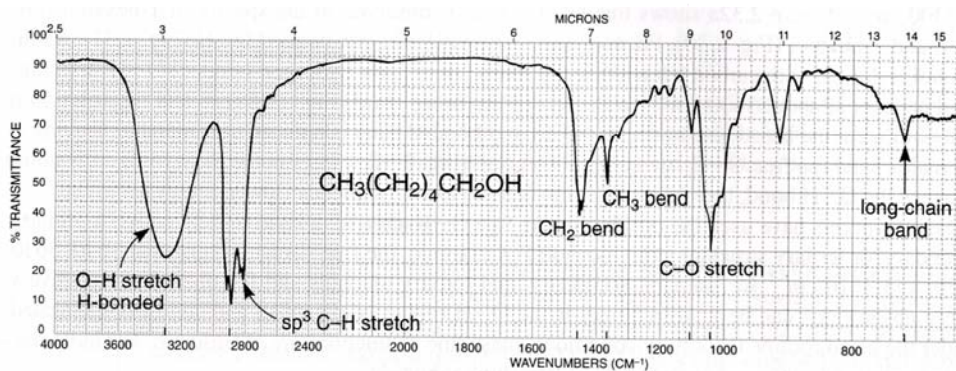
$\text{C}\equiv\text{C}$ stretch
~ 2150 cm^{-1} ,
but only when
asymmetric.



Characteristic Features in IR: Alcohols

O-H stretch 3650-3600 cm^{-1} if dilute (no H-bonding).

O-H stretch 3400-3300 cm^{-1} if H-bonded.

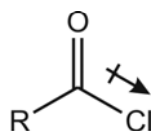


Characteristic Features in IR: Carbonyls

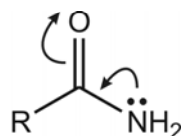
C=O stretch 1800-1600 cm^{-1} ; typically sharp and strong.
Very diagnostic.

Frequency strongly affected by substituents:

$\longleftarrow \text{cm}^{-1} \longrightarrow$							
1810	1800	1760	1735	1725	1715	1710	1690
Anhydride (band 1)	Acid chloride	Anhydride (band 2)	Ester	Aldehyde	Ketone	Carboxylic acid	Amide



inductive effect
raises bond frequency



resonance effect
lowers bond frequency