Nuclear Magnetic Resonance Spectroscopy Depends on Nuclear Spin

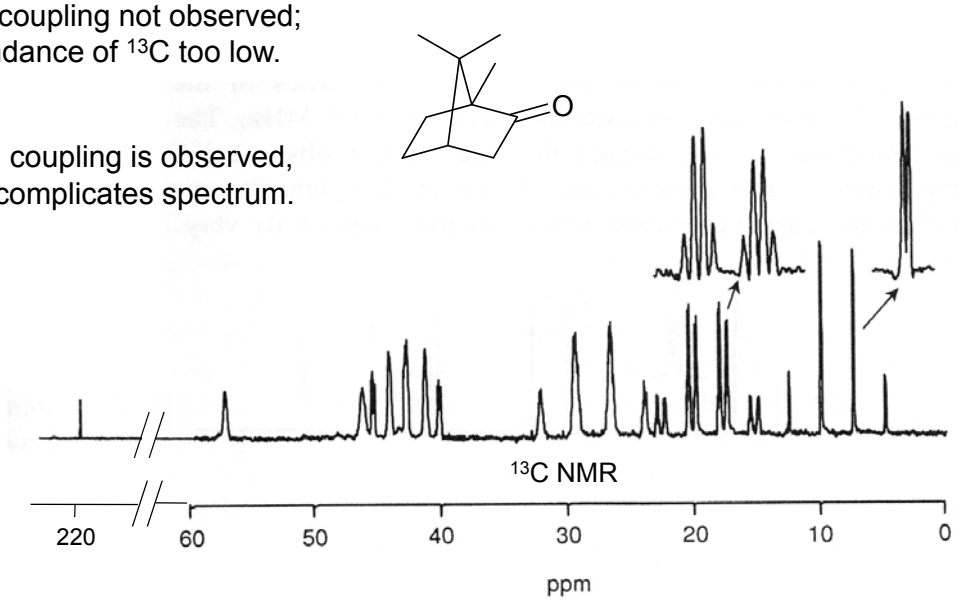
Nucleus	Spins	Isotope Abundance
^{1}H	±½	99.9%
^{12}C	0	98.9%
^{13}C	±½	1.1%
^{19}F	±½	100%
^{31}P	±½	100%

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

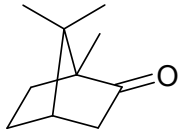
^{13}C NMR: A Problem With Coupling

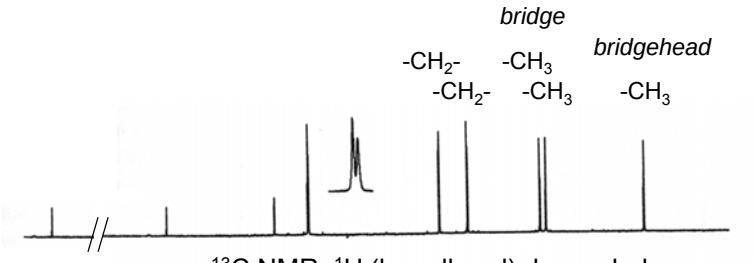
$^{1}H \leftarrow C$ coupling not observed; abundance of ^{13}C too low.

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



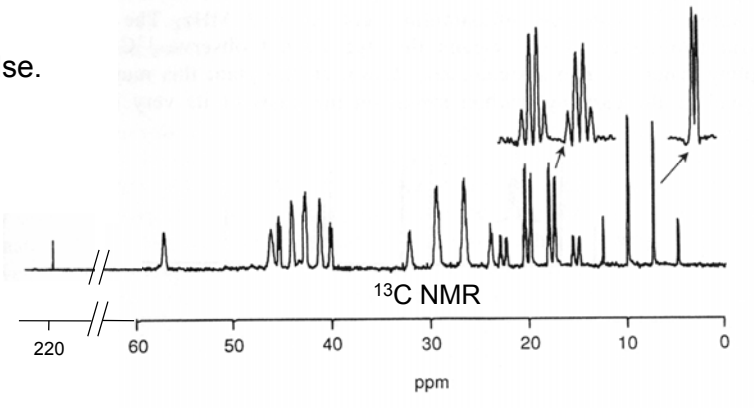
^{1}H-Decoupled ^{13}C NMR



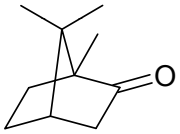


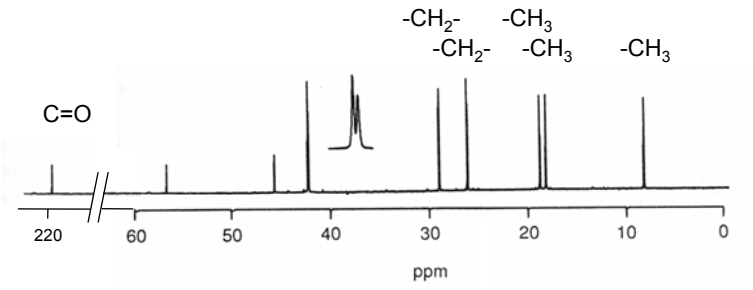
^{13}C NMR, ^{1}H (broadband) decoupled

Solution: Decoupling pulse.



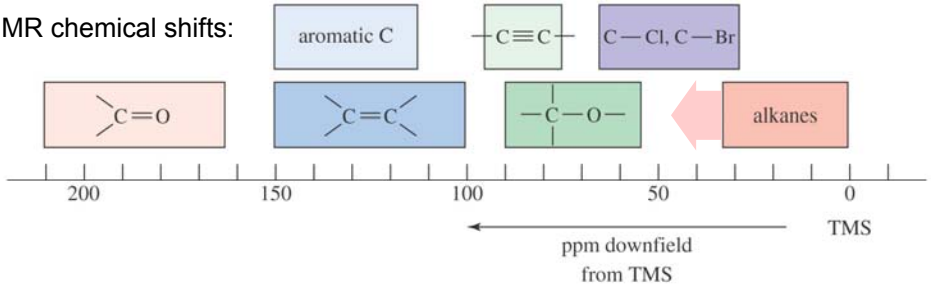
^{1}H-Decoupled ^{13}C NMR





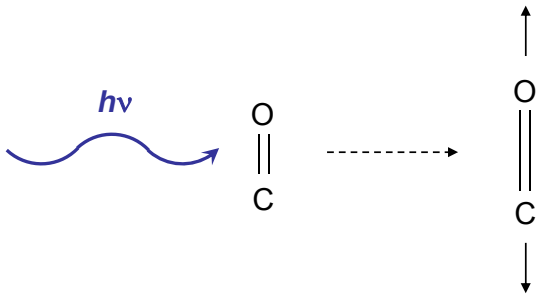
^{13}C NMR, ^{1}H (broadband) decoupled

Typical ^{13}C NMR chemical shifts:

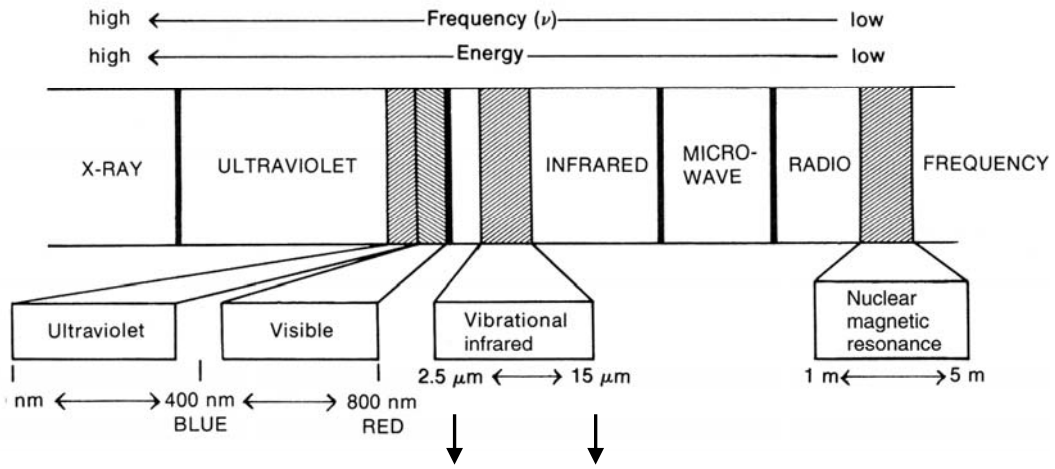


Infrared (IR) Spectroscopy

- 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



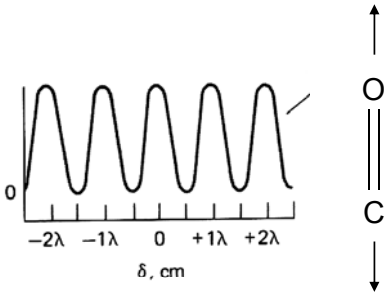
2.5 x 10^{-4} cm → 4000 cm^{-1}

1.5 x 10^{-3} cm → 660 cm^{-1}

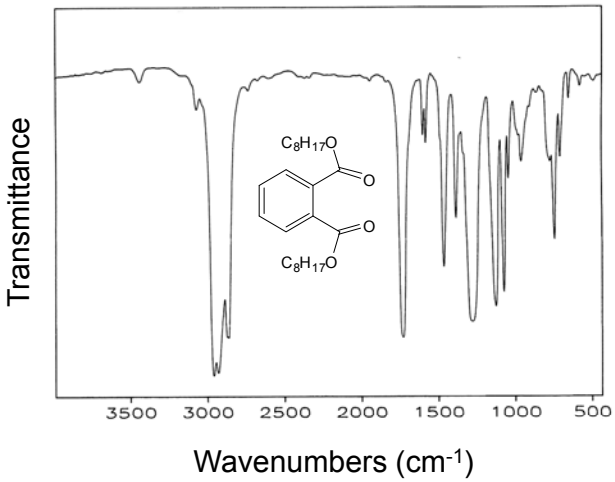
("wavenumbers"; 1/λ is proportional to energy)

IR Spectroscopy: Methods

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



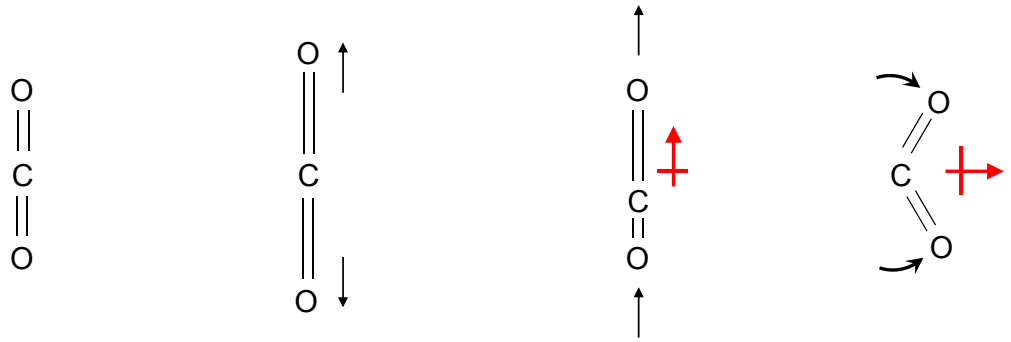
Molecules are mostly transparent to IR light, but when frequency matches a bond vibration, light doesn't pass through.



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

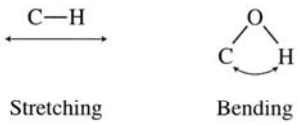
Frequency (cm^{-1})	Functional Group		Comments
3300	alcohol	O—H	always broad
	amine, amide	N—H	may be broad, sharp, or broad with spikes
	alkyne	≡C—H	always sharp, usually strong
3000	alkane	—C(—)—H	just below 3000 cm^{-1}
	alkene	=C(H)—	just above 3000 cm^{-1}
	acid	O—H	very broad
2200	alkyne	—C≡C—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

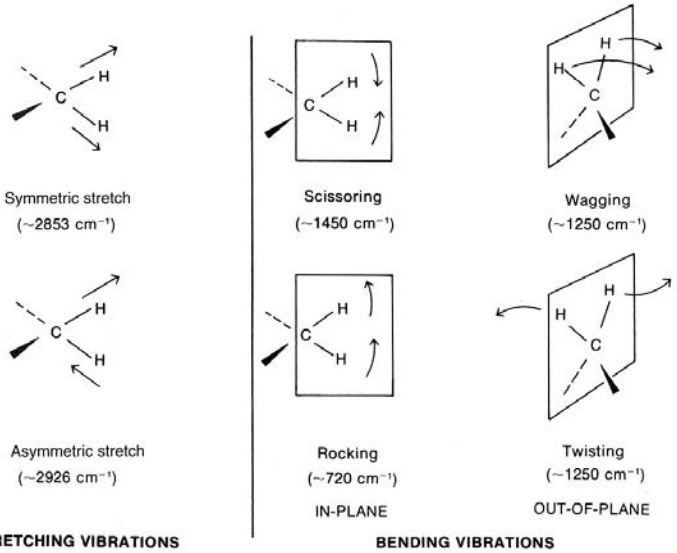
IR-Allowed C-H Vibrations

single modes



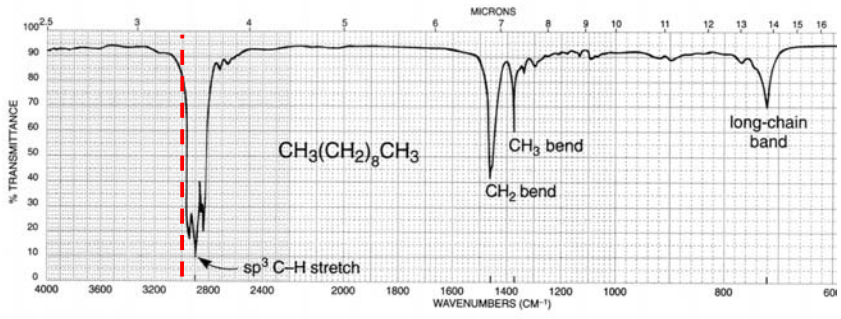
Stretching Bending

combination modes

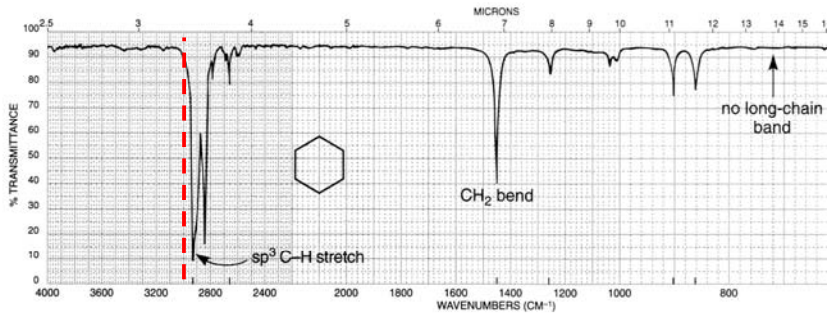


Characteristic Features in IR: Alkanes

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



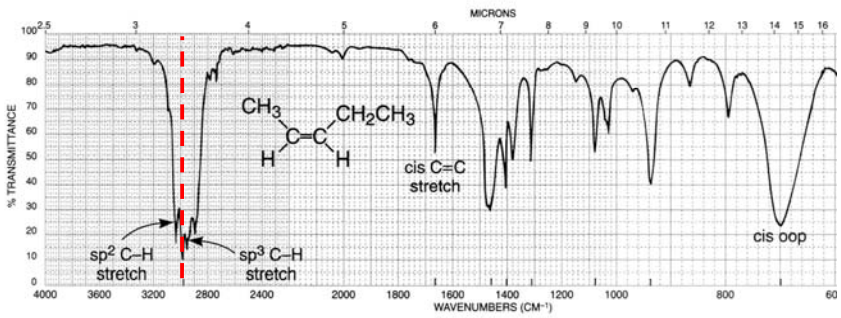
3000 cm^{-1}



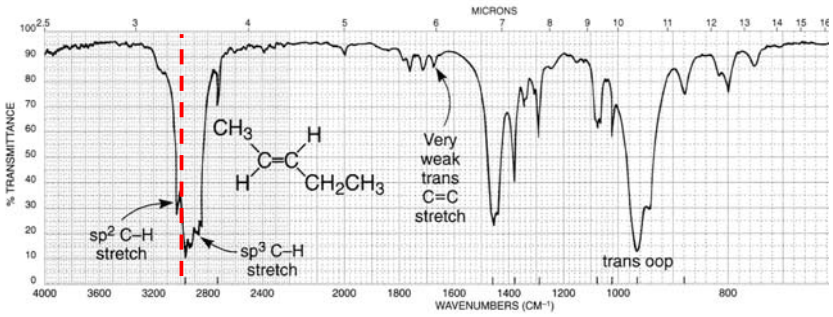
Characteristic Features in IR: Alkenes

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

C=C stretch ~ 1600-1660 cm^{-1}; affected by bond stereochemistry.



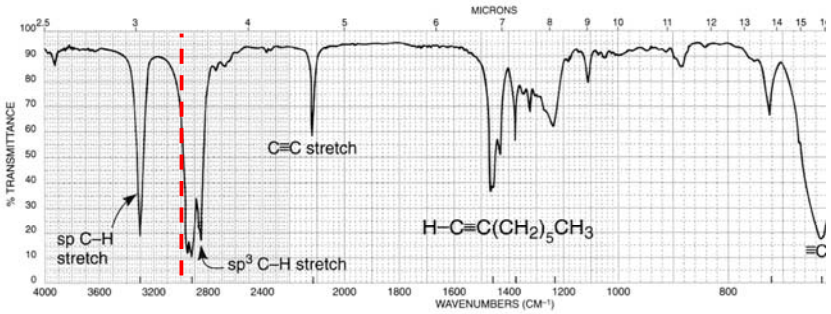
3000 cm^{-1}



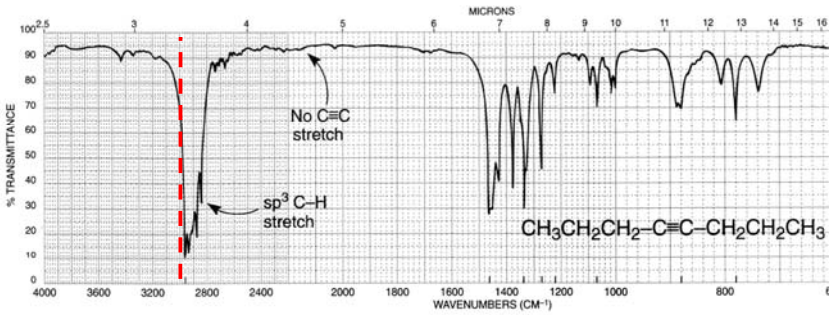
Characteristic Features in IR: Alkynes

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

C≡C stretch
~ 2150 cm^{-1},
but only when
asymmetric.



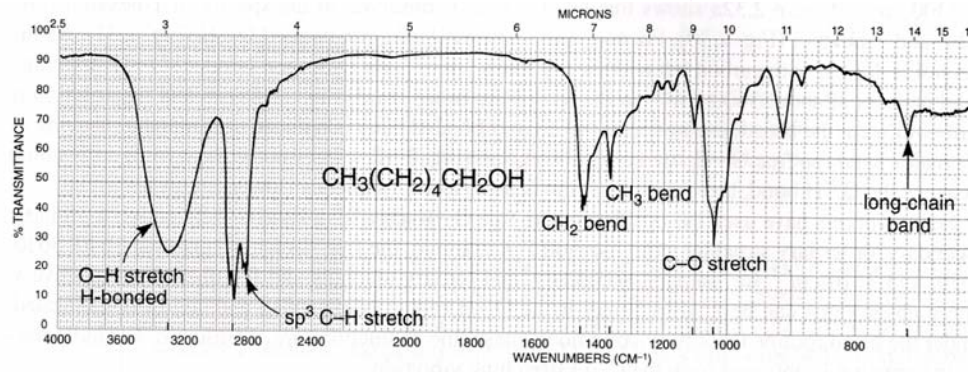
3000 cm^{-1}



Characteristic Features in IR: Alcohols

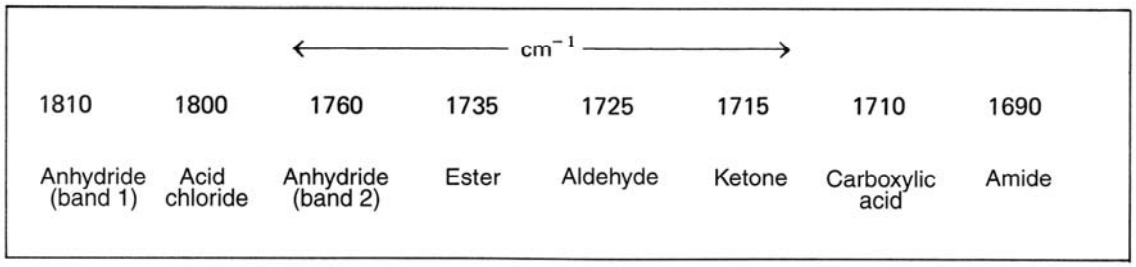
O-H stretch 3650-3600 cm^{-1} if dilute (no H-bonding).

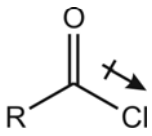
O-H stretch 3400-3300 cm^{-1} if H-bonded.



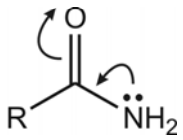
Characteristic Features in IR: Carbonyls

C=O stretch 1800-1600 cm^{-1}; typically sharp and strong.
Very diagnostic.
Frequency strongly affected by substituents:





inductive effect
raises bond frequency



resonance effect
lowers bond frequency