

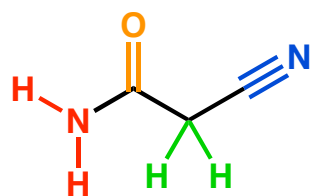


Use of IR spectroscopy

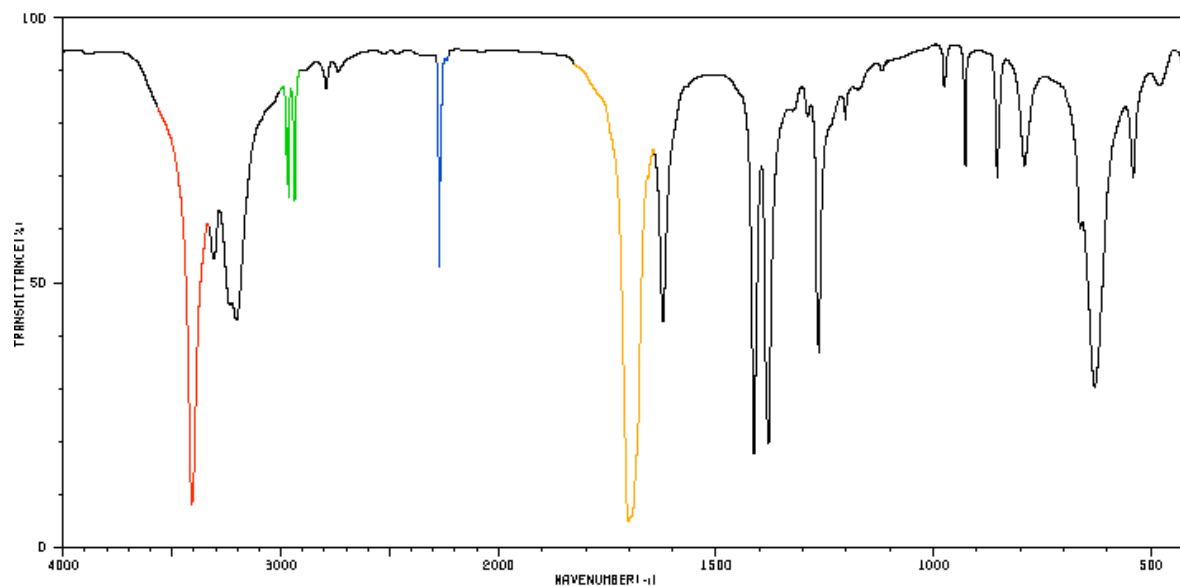
← energy to cause vibration →
4000 3000 2000 1500 1000 cm^{-1}

O—H	C≡C	change in scale	C=C	C—O
N—H	C≡N		C=O	C—F
C—H	C≡O			C—Cl
bonds to hydrogen	triple bonds		double bonds	single bonds

- 4 interesting areas to IR spectra (left)
- 1500-400 cm^{-1} = fingerprint region
- Individual to each molecule
- But not much useful information!



3500 - NH
2950 - CH
2270 - C≡N
1700 - C=O





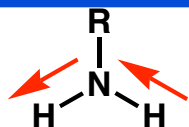
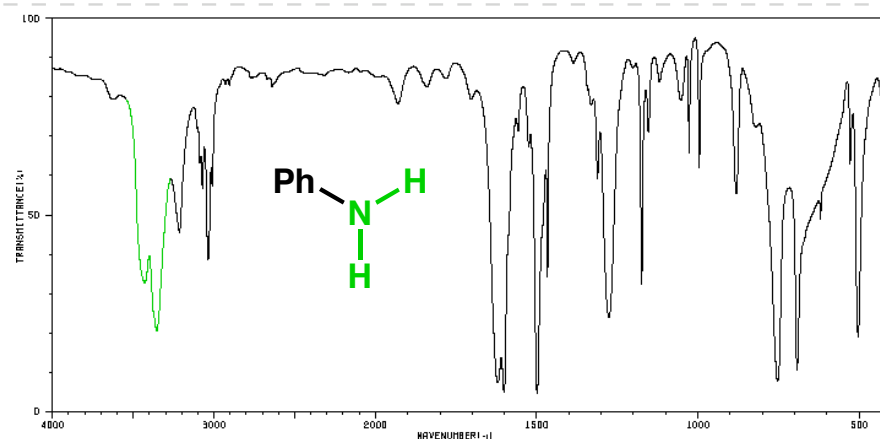
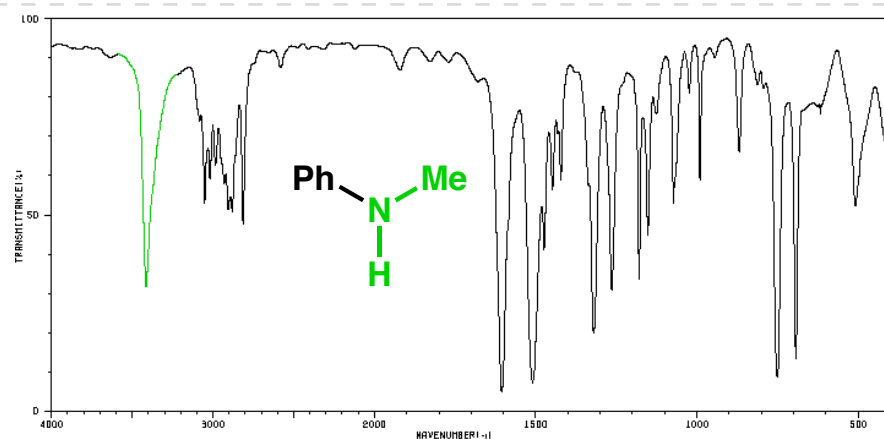
X-H Region

C-H	2900 - 3000 cm^{-1}
-----	------------------------------

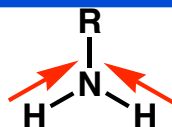
N-H	3300 - 3400 cm^{-1}
-----	------------------------------

O-H	3500 - 3600 cm^{-1}
-----	------------------------------

Reduced mass μ very similar for all
So order a result of bond strength
OH > NH > CH



anti-symmetric stretch
3400 cm^{-1}

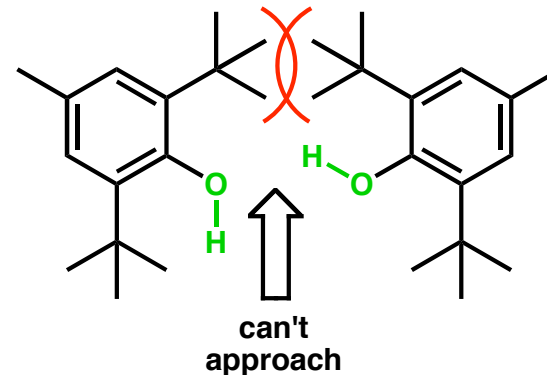
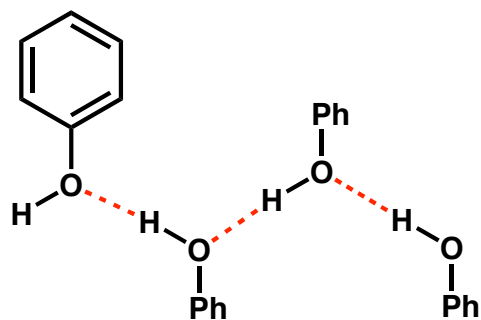
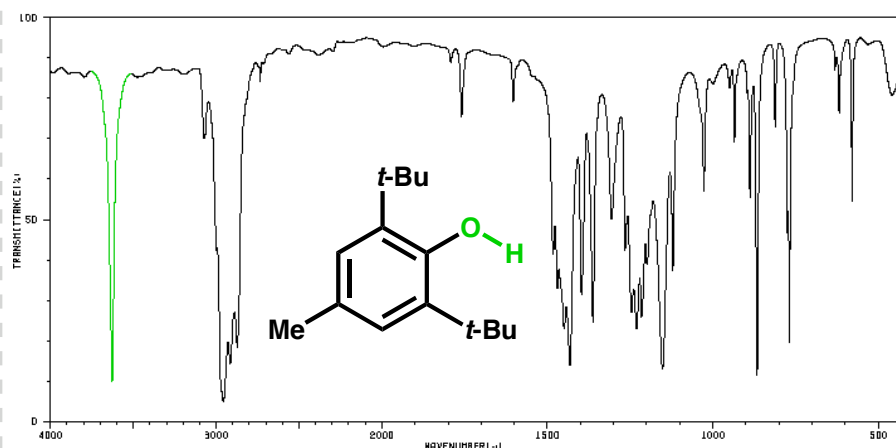
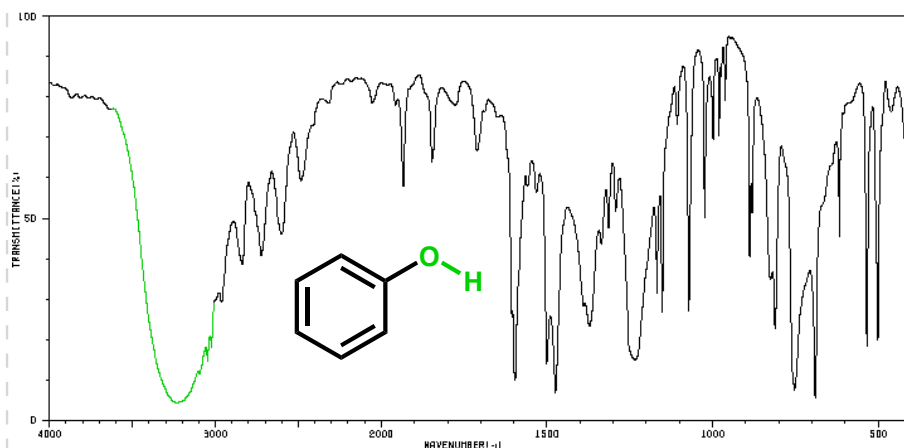


symmetric stretch
3300 cm^{-1}

- 2 N-H bonds in aniline act as one 'unit'
- Two possible vibrations so two peaks



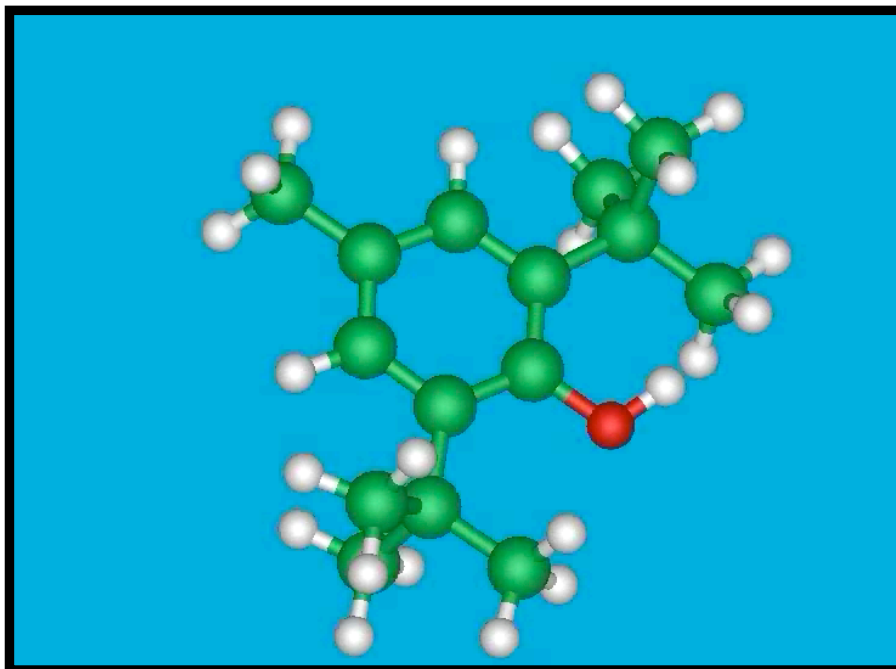
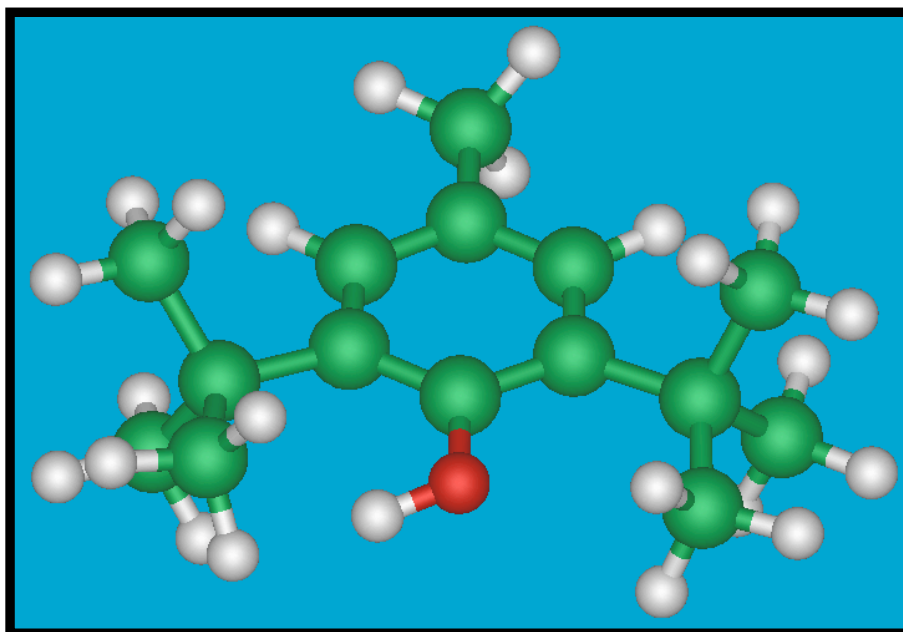
X-H: Hydrogen bonding



- H-bonds vary in strength and length
- They cause a weakening of X-H bonds
- The range of strengths leads to a range of absorptions



Butylated hydroxytoluene BHT



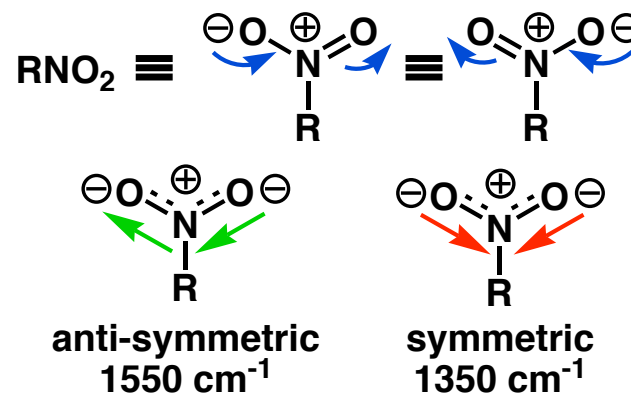
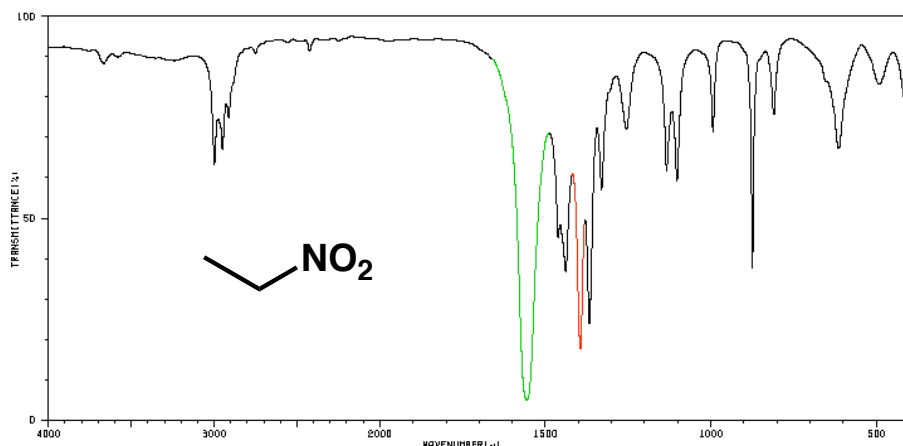
The steric bulk of the two *tert*-butyl groups prevents two molecules of BHT from hydrogen bonding with each other and we get a sharp peak in the IR spectrum



Double bond region

C=O carbonyl group	1900 – 1500 cm ⁻¹ strong
C=C alkene	1640 cm ⁻¹ weak
O–N=O nitro group	1500 & 1300 cm ⁻¹ 2 strong peaks

- Practically the most useful region in IR
- Certainly the most information



- Two peaks as two forms of stretch (like primary amine)
- Symmetric stretch weaker absorption as less change in dipole



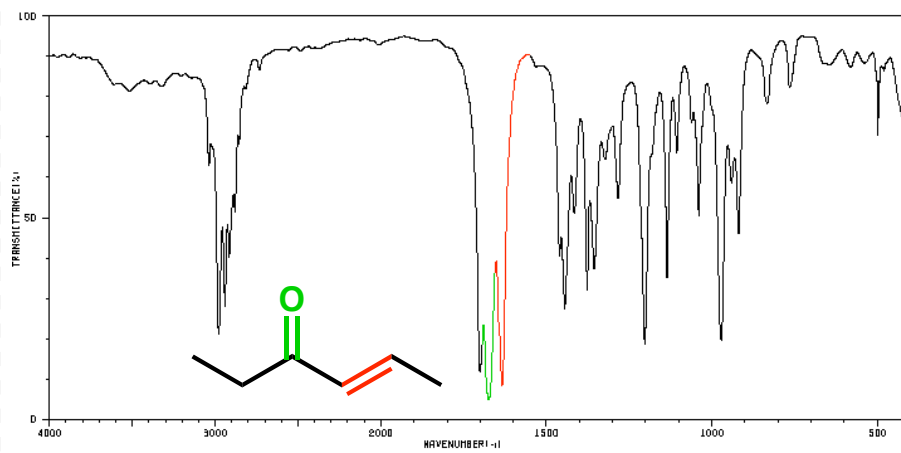
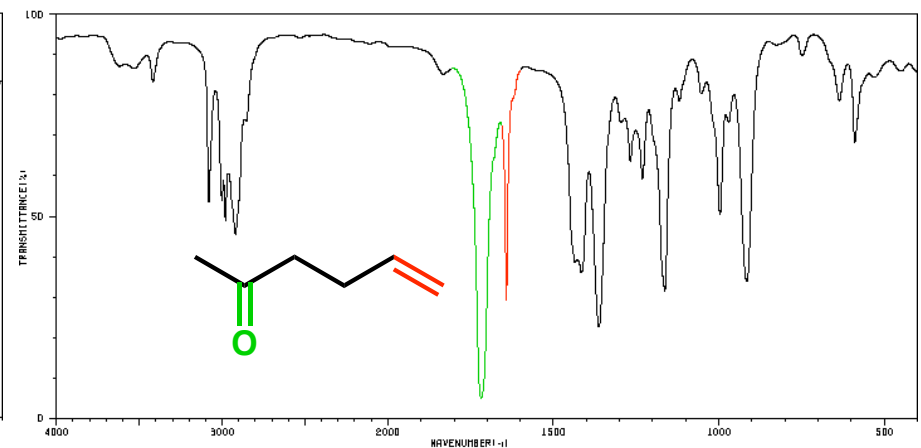
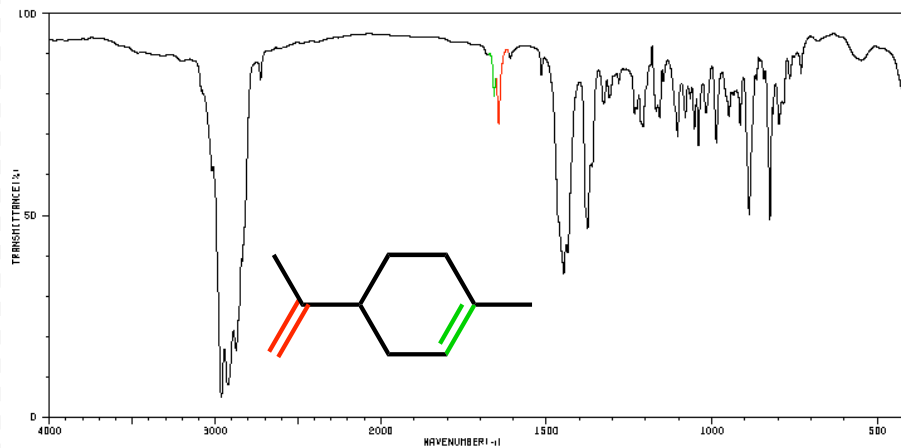
Alkenes

structure	wavenumber (cm ⁻¹)	comment
	1640 (m, sh)	m = medium sh = sharp
	1655 (m, sh)	More substituents the stronger the bond & higher absorption
	1660 - 1675 (w)	<ul style="list-style-type: none"> • More substituents = stronger bond • But less change in dipole moment so reduced intensity • Symmetrical alkenes close to no absorption

- sp² centres form stronger bonds as more s character ⇒ better orbital overlap
- C-H of alkene >3000 cm⁻¹
- C-H of alkyl <3000 cm⁻¹



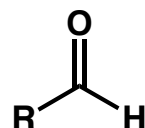
Examples of alkenes



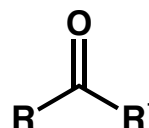
- Limonene - peaks weak as little change in dipole moment
- **Internal** alkene higher wavenumber due to substitution
- But less intense as less change in dipole moment
- Isolated C=O & C=C in normal positions (above)
- Conjugated / resonance lowers both as more single bond character BUT more intense as polarised



Carbonyl group (C=O) in IR

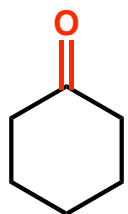


aldehydes
RCHO
1720 – 1725 cm^{-1}

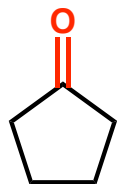


ketones
RCOR'
1710 – 1715 cm^{-1}

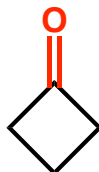
Aldehydes have stronger bonds than ketones - why?
Carbonyl functionality most useful in IR (in my opinion)



1715 cm^{-1}



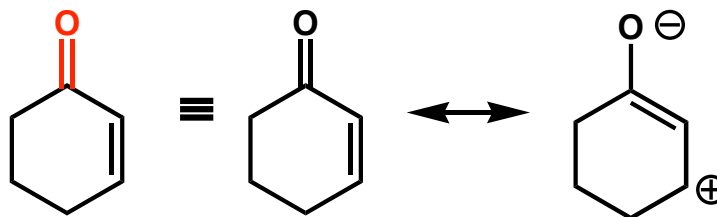
1745 cm^{-1}



1780 cm^{-1}

- As C=O gets more strained so bond gets stronger! But more reactive
- Angle less than 120° so needs more p character
- Leaves more s character in C=O so shorter and stronger bond

- Why weaker than normal?
- Delocalisation results in single bond character

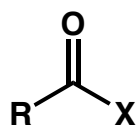


1690 cm^{-1}



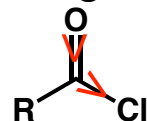
Carbonyl group (C=O) in IR II

Carboxylic acid derivatives



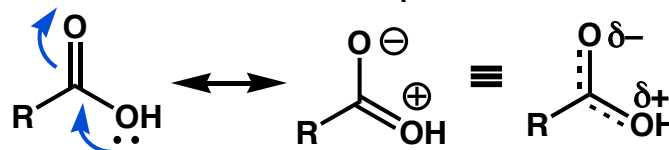
X = Cl 1815 cm⁻¹

Electronegative Cl drags electrons close making π bond shorter and stronger



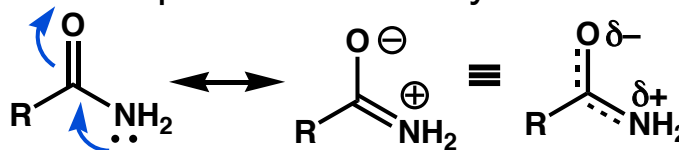
X = OH 1745cm⁻¹

Stronger than ketone due to electronegative oxygen. But delocalisation of lone pair weakens π bond.



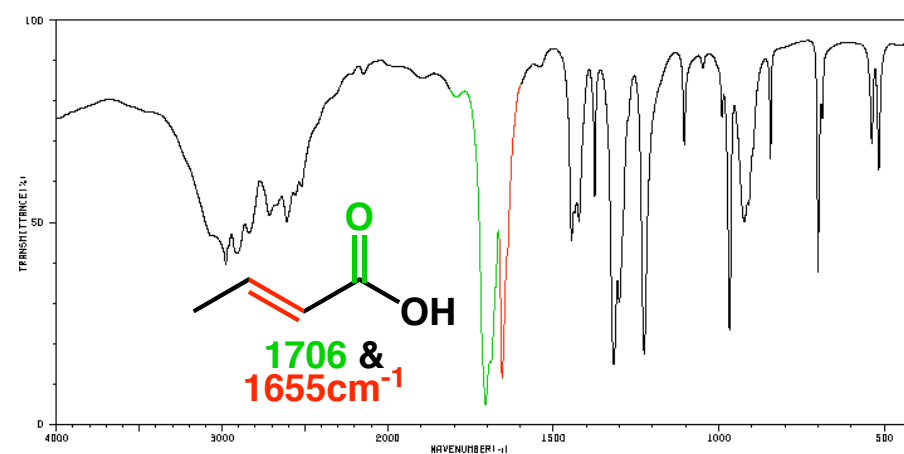
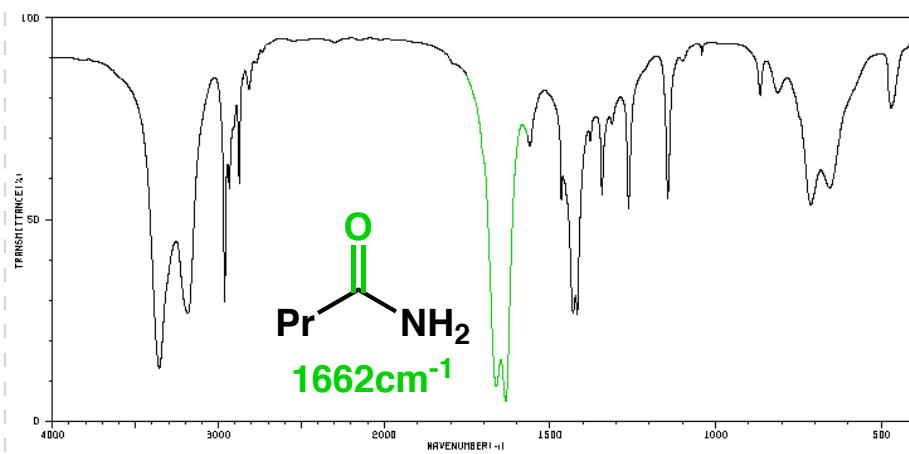
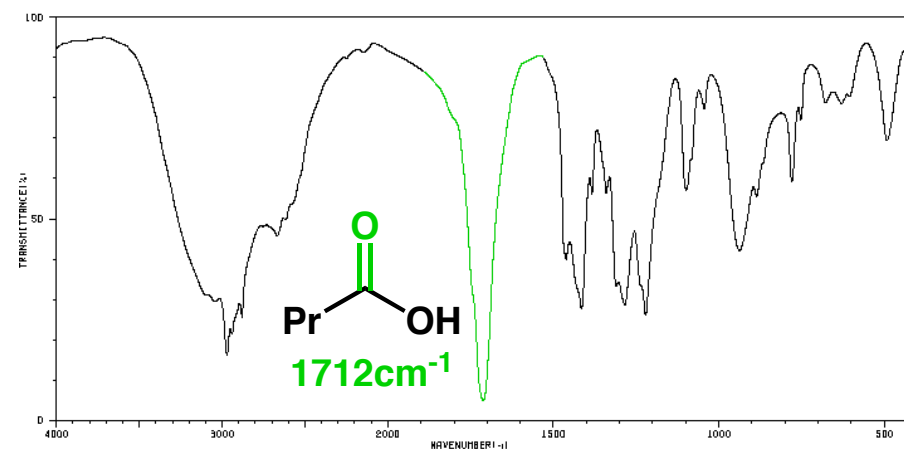
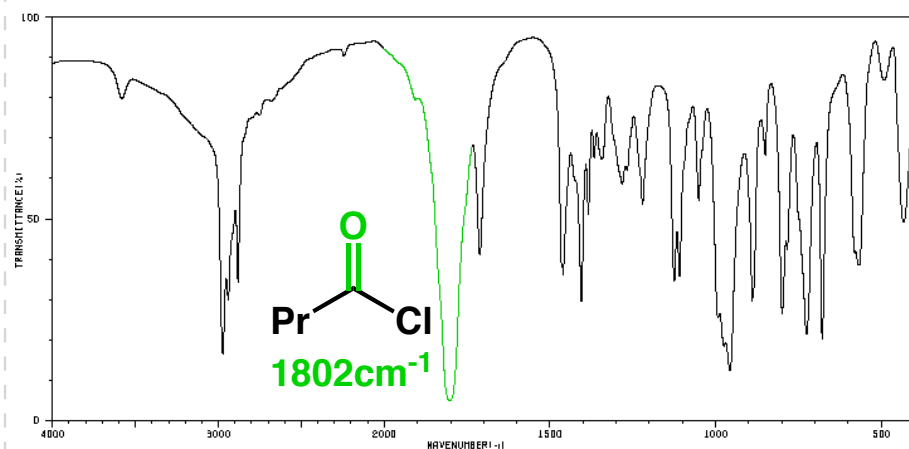
X = NH₂ 1650 cm⁻¹

Amides have even weaker π bond due to increased delocalisation. Nitrogen is less electronegative so donates lone pair more readily.





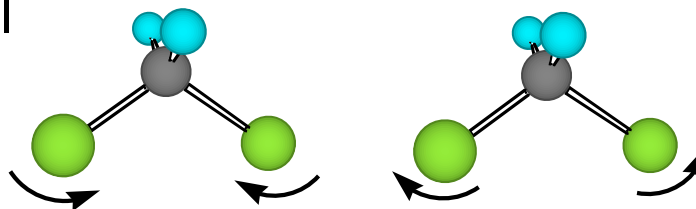
Carbonyl group: examples





Fingerprint region

- 1500 cm^{-1} or less is fingerprint region - unique to a molecule
- But dull C–C, C–N & C–O roughly same reduced mass and bond strength - so nothing distinctive
- Deformations (or bending) occurs at low energy as well
- Very few are useful



Summary of absorptions in IR spectra

Position of band	➔	reduced mass bond strength	light atoms - high frequency strong bond - high frequency
Strength of band	➔	change in dipole moment	large dipole - strong band
Width of band	➔	hydrogen bonding	strong H bond - weak band



Correlation table

