

# Organic Identification

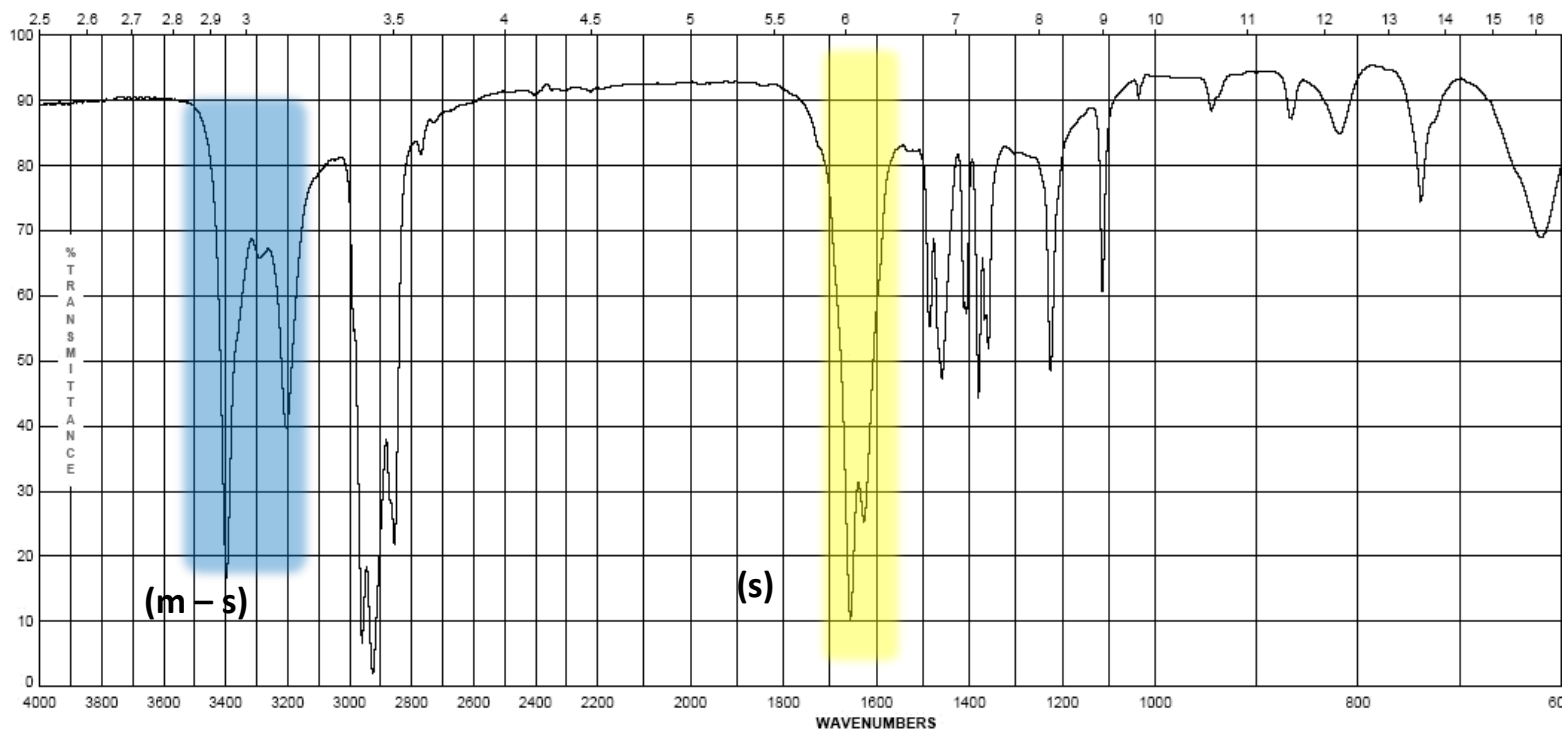
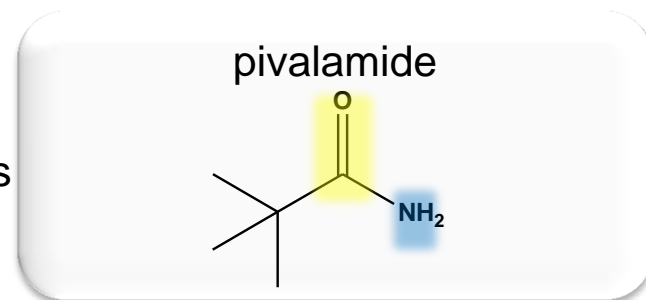
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# Infrared Spectroscopy

## 16. Amides

- Display features of amines and carbonyl compounds
- C=O stretch at 1640-1680  $\text{cm}^{-1}$
- If the amide is primary ( $-\text{NH}_2$ ) the N-H stretch occurs from 3200-3500  $\text{cm}^{-1}$  as a doublet
- If the amide is secondary ( $-\text{NHR}$ ) the N-H stretch occurs at 3200-3500  $\text{cm}^{-1}$  as a sharp singlet

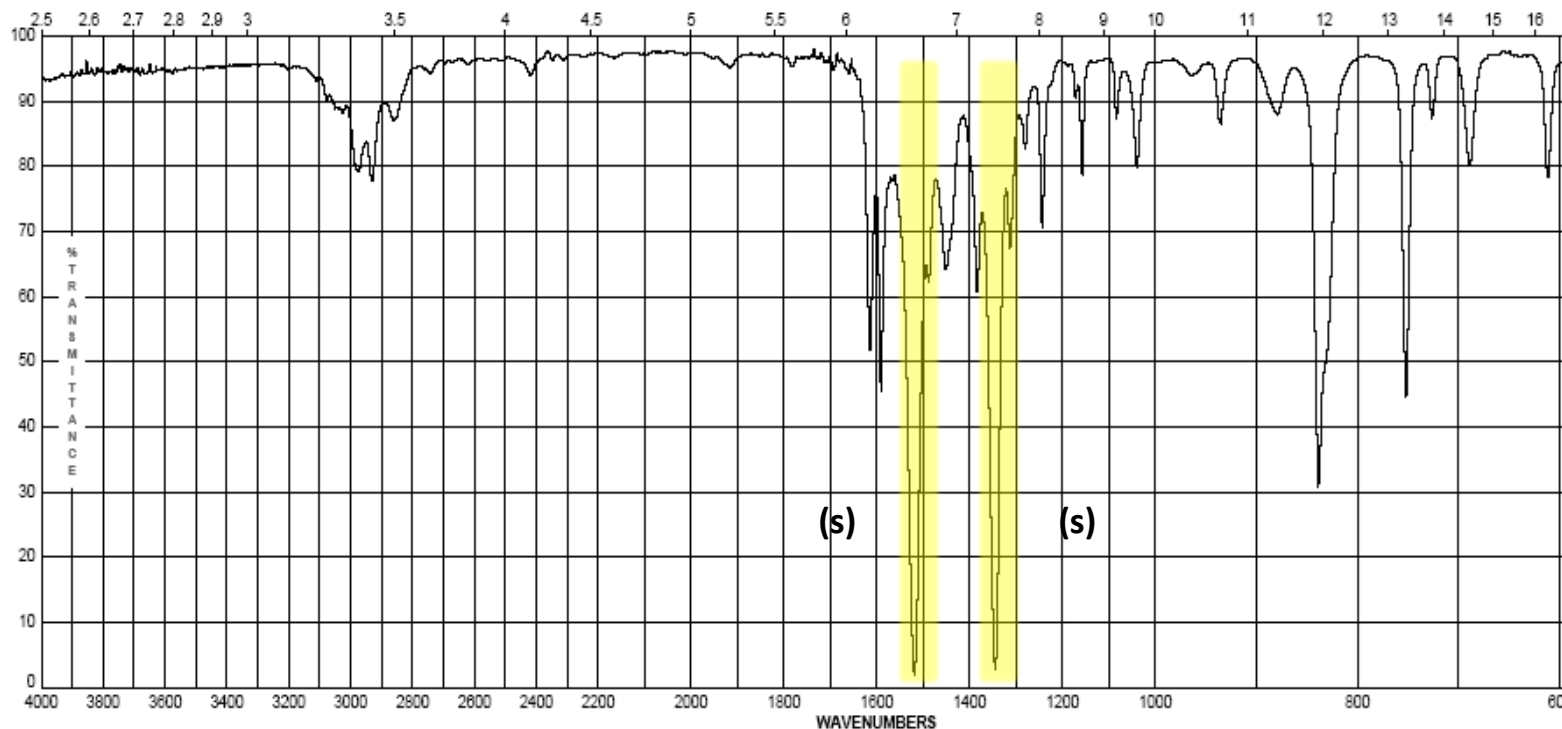
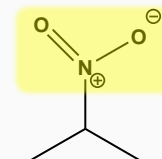


# Infrared Spectroscopy

## 17. Nitro group (-NO<sub>2</sub>)

- Proper Lewis structure gives a bond order of 1.5 from nitrogen to each oxygen
- Two bands are seen (symmetric and asymmetric) at 1300-1380 cm<sup>-1</sup> and 1500-1570 cm<sup>-1</sup>
- This group is a strong resonance withdrawing group and is itself vulnerable to resonance effects

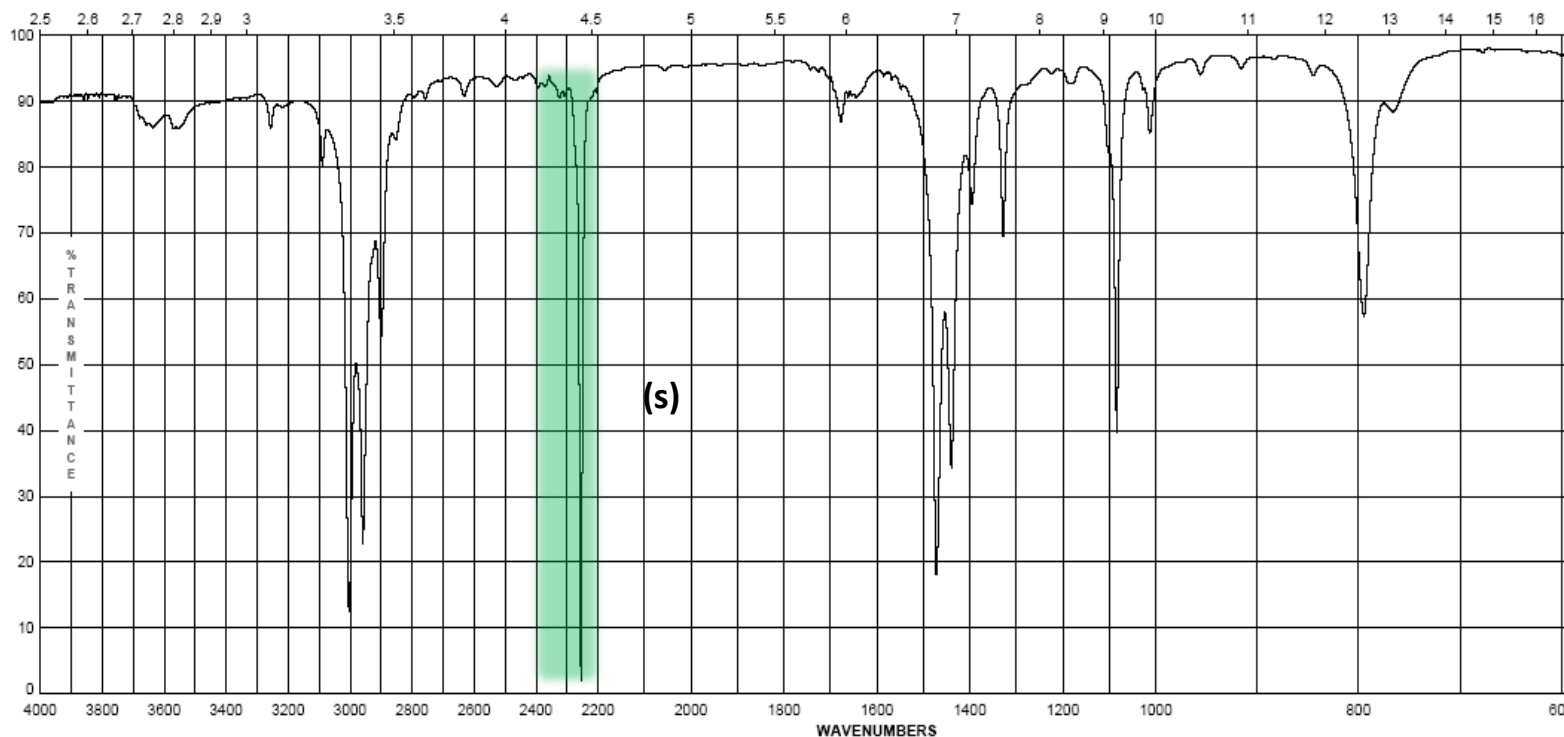
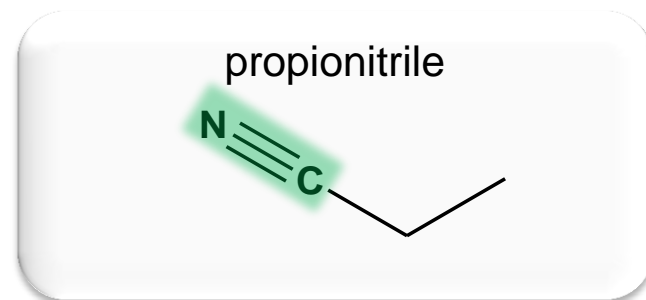
2-nitropropane



# Infrared Spectroscopy

## 18. Nitriles (the cyano- or $-\text{C}\equiv\text{N}$ group)

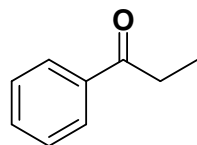
- Principle group is the carbon nitrogen triple bond at  $2100\text{-}2280\text{ cm}^{-1}$
- This peak is usually much more intense than that of the alkyne due to the electronegativity difference between carbon and nitrogen



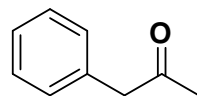
# Infrared Spectroscopy

## Effects on IR bands

- Conjugation** – by resonance, conjugation lowers the energy of a double or triple bond. The effect of this is readily observed in the IR spectrum:

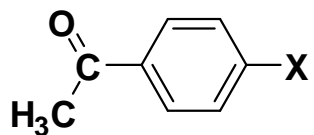


1684  $\text{cm}^{-1}$   
C=O

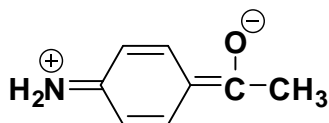


1715  $\text{cm}^{-1}$   
C=O

- Conjugation will lower the observed IR band for a carbonyl from 20-40  $\text{cm}^{-1}$  provided conjugation gives a strong resonance contributor

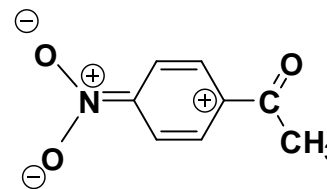


X =	NH <sub>2</sub>	CH <sub>3</sub>	Cl	NO <sub>2</sub>	
	1677	1687	1692	1700	$\text{cm}^{-1}$



**Strong resonance contributor**

vs.



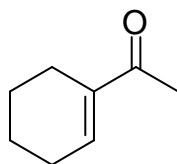
**Poor resonance contributor  
(cannot resonate with C=O)**

- Inductive effects are usually small, unless coupled with a resonance contributor (note  $-\text{CH}_3$  and  $-\text{Cl}$  above)

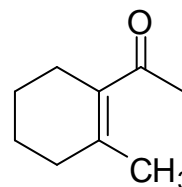
# Infrared Spectroscopy

## Effects on IR bands

2. **Steric effects** – usually not important in IR spectroscopy, unless they reduce the strength of a bond (usually  $\pi$ ) by interfering with proper orbital overlap:



C=O:  $1686\text{ cm}^{-1}$



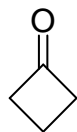
C=O:  $1693\text{ cm}^{-1}$

- Here the methyl group in the structure at the right causes the carbonyl group to be slightly out of plane, interfering with resonance

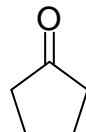
3. **Strain effects** – changes in bond angle forced by the constraints of a ring will cause a slight change in hybridization, and therefore, bond strength



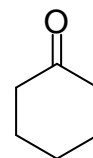
$1815\text{ cm}^{-1}$



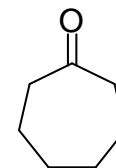
$1775\text{ cm}^{-1}$



$1750\text{ cm}^{-1}$



$1715\text{ cm}^{-1}$



$1705\text{ cm}^{-1}$

- As bond angle decreases, carbon becomes more electronegative, as well as less  $sp^2$  hybridized (bond angle  $< 120^\circ$ )

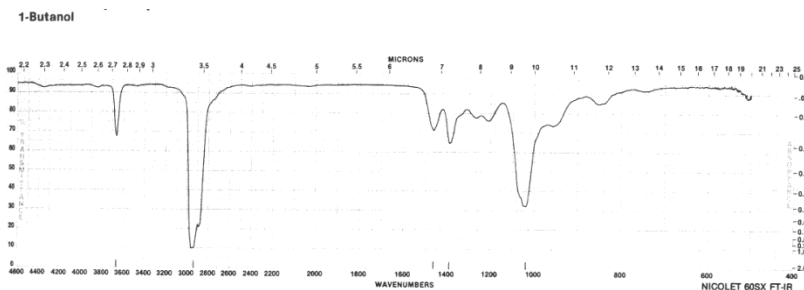
# Infrared Spectroscopy

## Effects on IR bands

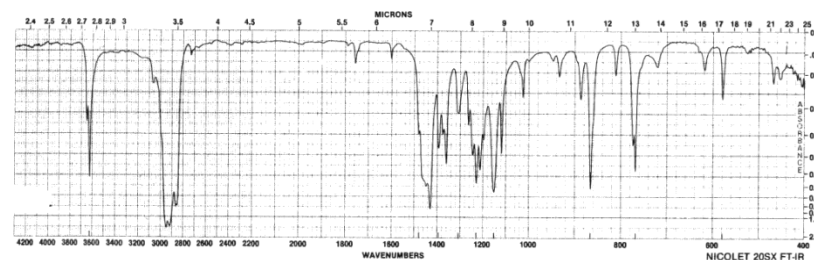
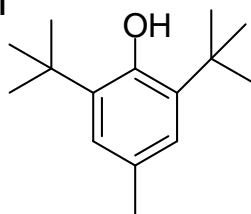
### 4. Hydrogen bonding

- Hydrogen bonding causes a broadening in the band due to the creation of a continuum of bond energies associated with it
- In the solution phase these effects are readily apparent; in the gas phase where these effects disappear or in lieu of steric effects, the band appears as sharp as all other IR bands:

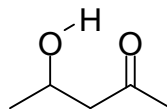
Gas phase spectrum of 1-butanol



Steric hindrance to H-bonding in a di-*tert*-butylphenol



- H-bonding can interact with other functional groups to lower frequencies



C=O; 1701 cm<sup>-1</sup>