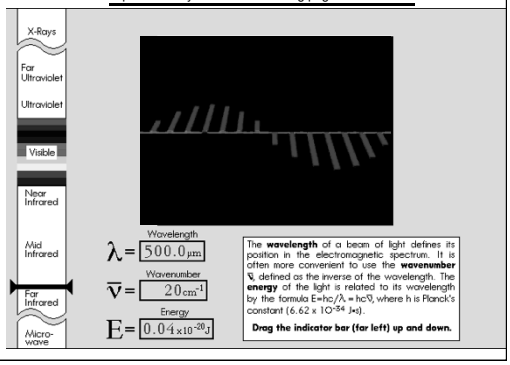
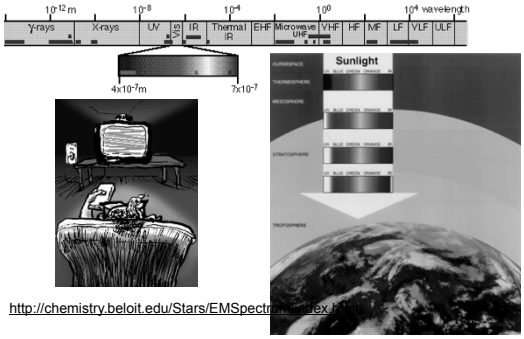
Infrared Spectroscopy

Electromagnetic Radiation: Light, Energy, Heat

IR Tutor: http://chemistry.beloit.edu/Warming/pages/infrared.html

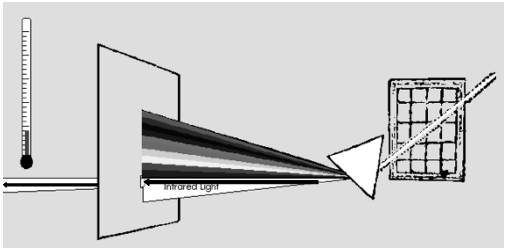


What do the sun's energy, a molecule's shape and a TV remote have to do with greenhouse gases?

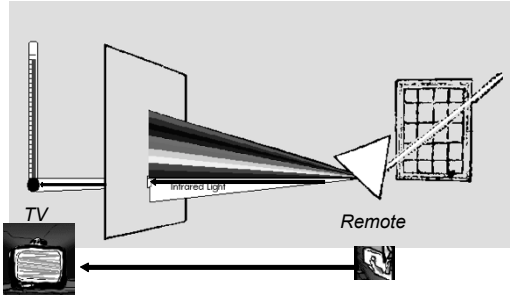


http://chemistry.beloit.edu/Stars/EMSpectr

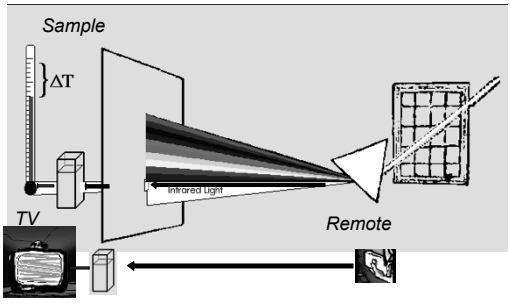
Infrared Absorbance



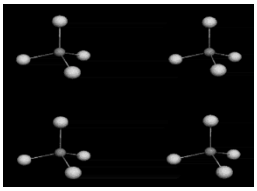
Infrared Absorbance



Infrared Absorbance



Infrared Absorbance & Molecular Vibrations for CCl_4 Stretching & Bending



Assignment

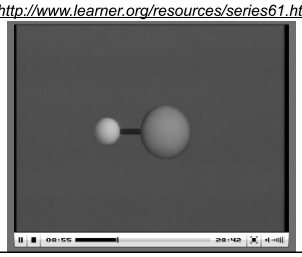
View: http://www.learner.org/resources/series61.html

#10 Signals from Within

[3:35-8:55] Spectroscopy

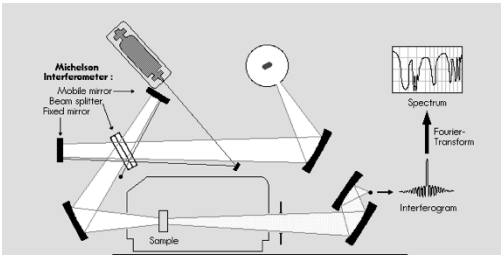
[8:55-20:29] Infrared Spectroscopy

http://www.learner.org/resources/series61.html



Infrared Spectroscopy

Infrared Absorbance



IR- Empirical Comparisons

Identifying functional groups in organic molecules

Analyzing Structure: Functions & Infrared Spectra

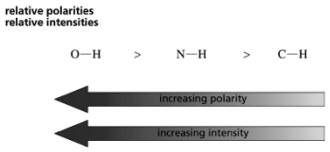
The molecular formula is a critical piece of information, which limits the functional possibilities.

The presence & absence of absorption bands must be considered in identifying a possible structure in IR spectroscopy. Empiricism is critical to successful identification.

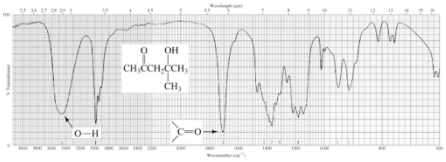
NOTE: Bonds which lack dipole moments are not detected.

A bond must have a dipole or an induced dipole in order to have an absorbance in the IR spectrum.

When the bond stretches, the increasing distance between the atoms increases the dipole moment. Therefore, the greater the dipole, the more intense the absorption. (i.e., The greater the molar extinction coefficient (ε) in Beer's law, A = εbc.



An Infrared Spectrum

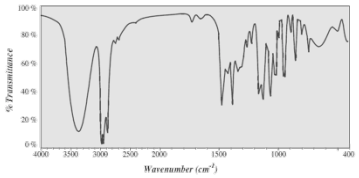


The peaks are quantized absorption bands corresponding to molecular stretching and bending vibrations

IR Spectra / Interpretation

Each signal in an IR spectrum has three important characteristics: WAVENUMBER (*frequency, which is proportional to energy*), INTENSITY, and SHAPE.

WAVENUMBER is the most important of the three, and every signal ***does not*** *need to be considered*



IR Interpretation: Wavenumber

- The WAVENUMBER for a stretching vibration depends on the bond strength and the mass of the atoms; bonded together

$$\tilde{\nu} = \left(\frac{1}{2\pi c}\right)\left(\frac{f}{m_{red}}\right)^{\frac{1}{2}}$$

force constant (bond strength)

$$\text{reduced mass} = \left(\frac{m_1 m_2}{m_1 + m_2}\right)$$

- Do bonds between heavier atoms absorb higher or lower energy (Wavenumber) for their respective stretching vibrations?

IR Interpretation: Wavenumber

$$\tilde{\nu} = \left(\frac{1}{2\pi c}\right)\left(\frac{f}{m_{red}}\right)^{\frac{1}{2}}$$

force constant (bond strength)

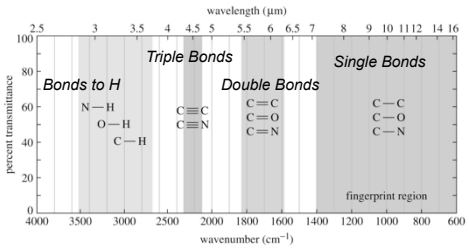
$$\text{reduced mass} = \left(\frac{m_1 m_2}{m_1 + m_2}\right)$$

C—H	C—D	C—O	C—Cl
~ 3000 cm^{-1}	~ 2200 cm^{-1}	~ 1100 cm^{-1}	~ 700 cm^{-1}

C≡N	C=N	C—N
~ 2200 cm^{-1}	~ 1600 cm^{-1}	~ 1100 cm^{-1}

IR Interpretation: Wavenumber

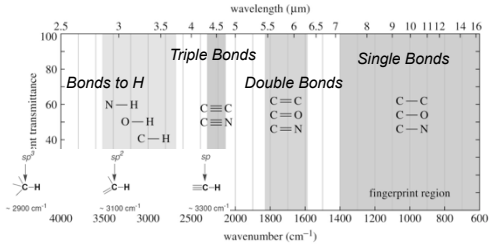
- Wavenumber relates to the relative strengths and polarity of the bonds.



- More energy is absorbed by stronger more polar bonds.

IR Interpretation: Wavenumber

- Wavenumber relates to the relative strengths and polarity of the bonds.



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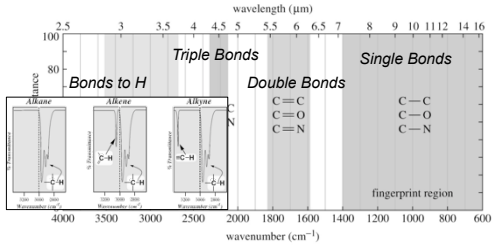


- More energy is absorbed by stronger more polar bonds.

Infrared Spectroscopy

Region of infrared that is most useful lies between 2.5-16 μm (4000-625 cm^{-1})

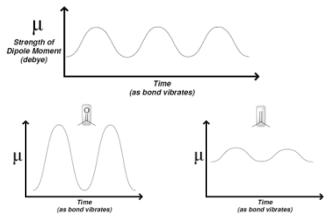
depends on transitions between vibrational energy states

Stretching: higher energy / higher wave number (cm^{-1})

Bending: lower energy / lower wave number (cm^{-1})

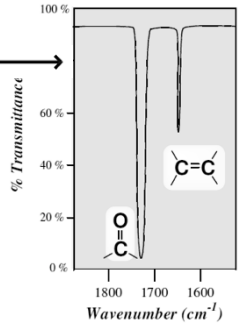
IR Interpretation: Intensity

- When a bond stretches, its dipole moment (μ) oscillates. Where the distance between the partial charges (*e*) varies: $\mu = e \times d$



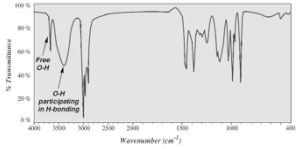
IR Interpretation: Intensity

- C=O is more polar than C=C and its signal more intense that a comparable C=C stretching absorbance.
- NOTE: A symmetrical molecule with a completely nonpolar C=C bond, eg. 2,3-dimethyl-2-butene, does not have a peak in the 1500–2000 cm^{-1} region.



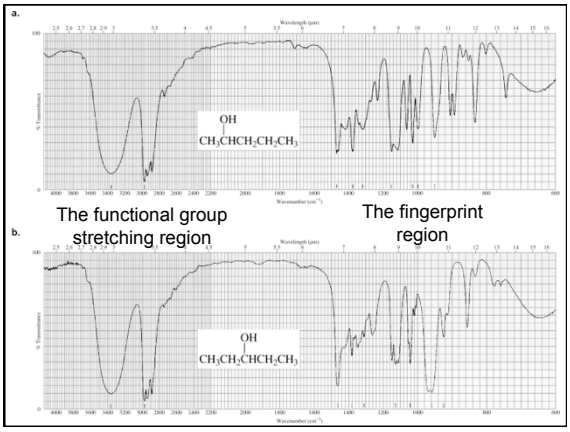
The wavenumber (energy/ frequency) and the intensity of the absorption band also depends on the concentration of solution from Beer's law, A = εbc.

It is easier to stretch an O–H bond if it is Hydrogen Bonded.



Important IR Stretching Frequencies

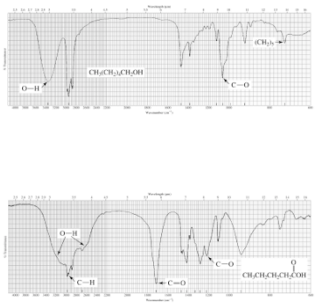
Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium



Infrared Absorption Frequencies

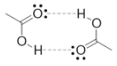
Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
O—H (alcohols)	3200-3600
O—H (carboxylic acids)	3000-3100
N—H	3350-3500

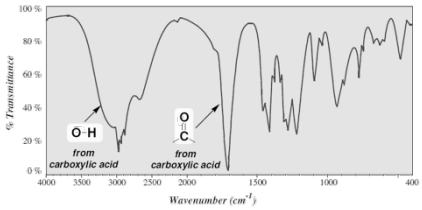
First examine the absorption bands in the vicinity of 4000-3000 cm^{-1}



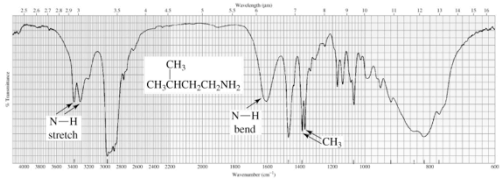
IR Interpretation: Shape

- H-bonding is often pronounced in carboxylic acids, because they can form H-bonding dimers.



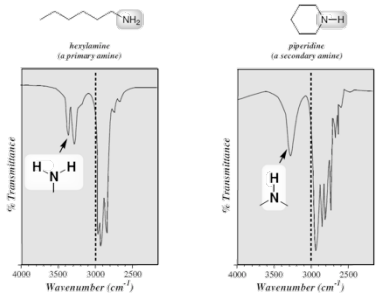


IR Spectrum of a Primary Amine(1°)



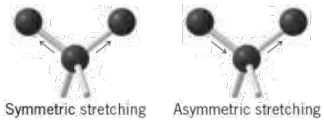
The N–H bending vibration occurs at ~1600 cm^{-1}

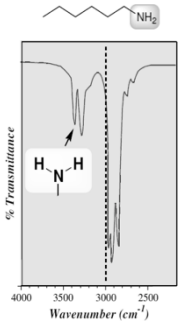
IR Interpretation: Shape



IR Interpretation: Shape

- The two N–H signals for a primary amine is the result of each N–H bond giving a different signals from stretching in two different ways.





Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

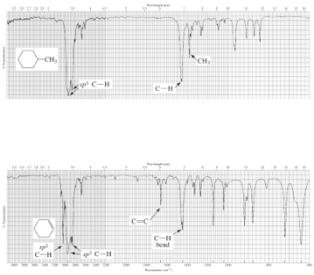
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp C—H	3310-3320
sp^2 C—H	3000-3100
sp^3 C—H	2850-2950
sp^2 C—O	1200
sp^3 C—O	1025-1200

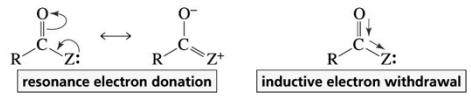
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (multiple bonds)	
C=C	1620-1680
—C≡C—	2100-2200
—C≡N	2240-2280

Some hydrocarbon absorption bands



Structural Components & Functional Differences:



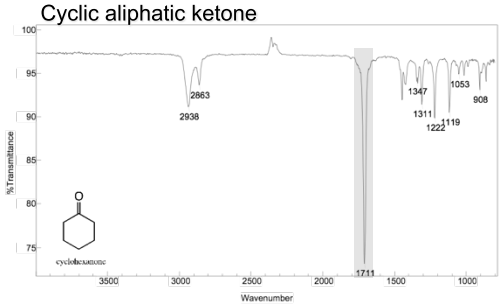
The nitrogen of an amide is less electronegative than the oxygen of an ester.

Therefore the amide has a longer (weaker) C=O bond (1680-1700 cm^{-1}) and the ester (1730-1750 cm^{-1}) is shorter (stronger).

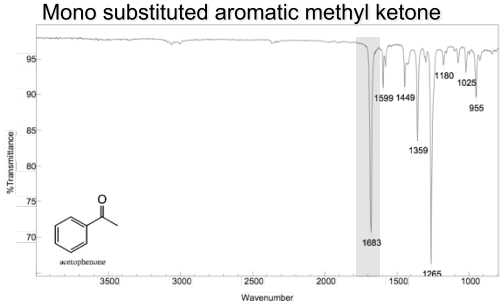
Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (carbonyl groups)	
Aldehydes and ketones	1710-1750
Carboxylic acids	1700-1725
Acid anhydrides	1800-1850 and 1740-1790
Esters	1730-1750
Amides	1680-1700

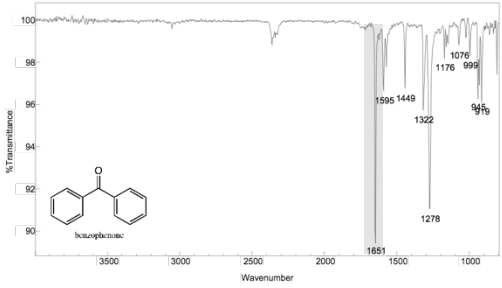
Cyclic aliphatic ketone



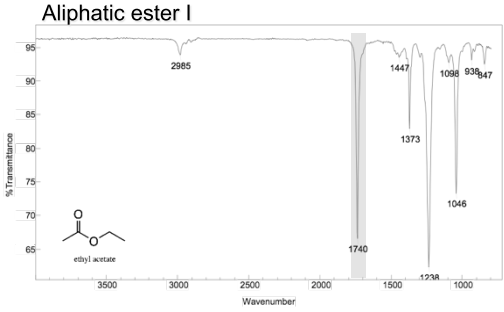
Mono substituted aromatic methyl ketone



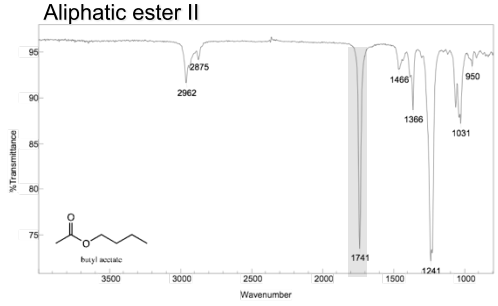
Mono substituted aromatic ketone



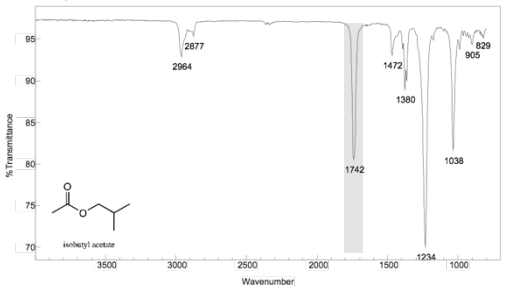
Aliphatic ester I



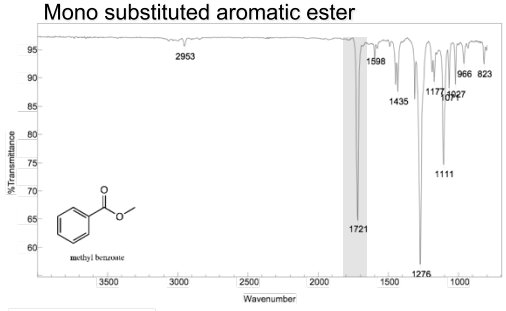
Aliphatic ester II



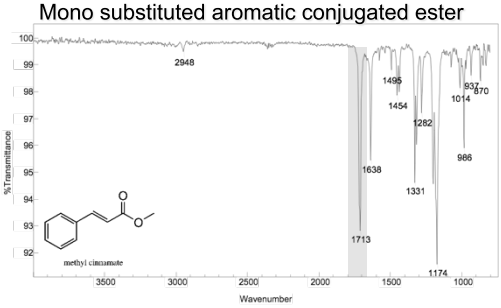
Aliphatic ester III



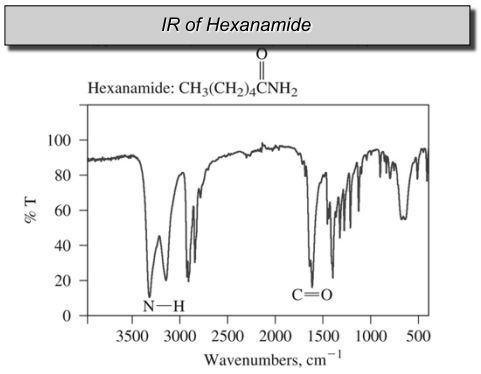
Mono substituted aromatic ester



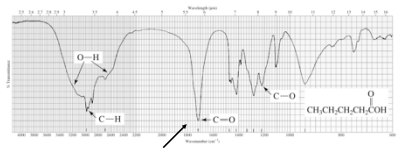
Mono substituted aromatic conjugated ester



IR of Hexanamide



What would theoretically explain the difference in the C=O stretching absorbances between an anhydride 1800-1850 cm^{-1} and 1740-1790 cm^{-1} *and a carboxylic acid* 1700-1725 cm^{-1} *?*



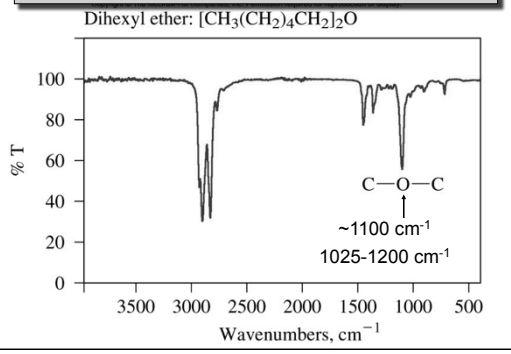
~1725 cm^{-1}

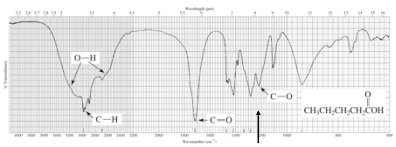
1700-1725 cm^{-1}

Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Stretching vibrations (single bonds)	
sp^2 C—O	1200
sp^3 C—O	1025-1200

Dihexyl Ether

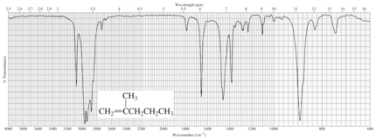




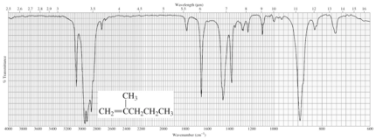
~1200 cm^{-1}

Infrared Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Bending vibrations of alkenes	
$RCH{=}CH_2$	910-990
$R_2C{=}CH_2$	890
cis-$RCH{=}CHR'$	665-730
trans-$RCH{=}CHR'$	960-980
$R_2C{=}CHR'$	790-840



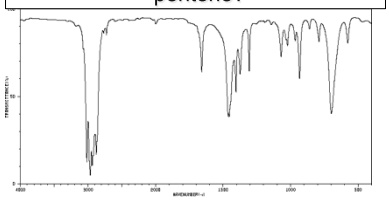
wavenumber (cm^{-1})	assignment
3075	?
2950	?
1650 and 890	?



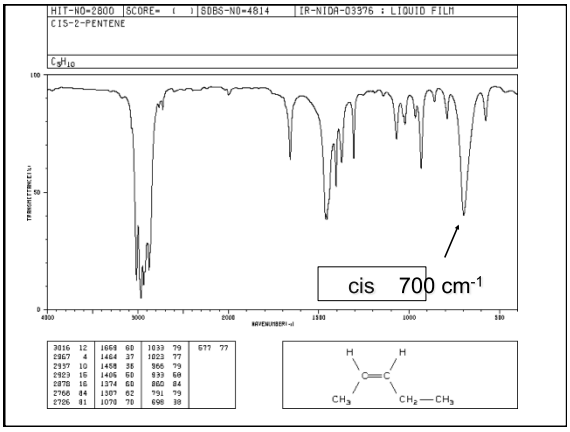
wavenumber (cm^{-1})	assignment
3075	*sp*^{2} CH
2950	*sp*^{3} CH
1650 and 890	a terminal alkene with two substituents

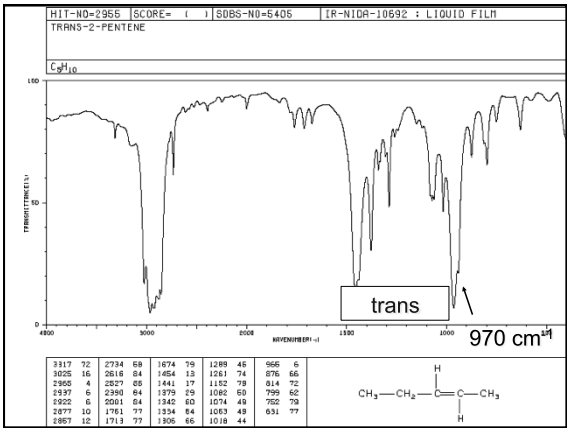
Question

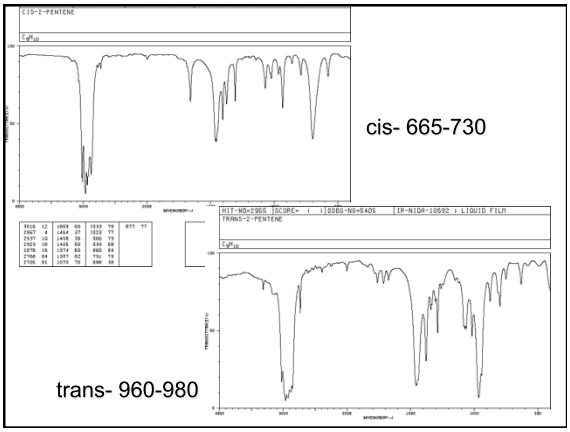
Is the following IR of cis or trans 2 -pentene?



A) cis B) trans

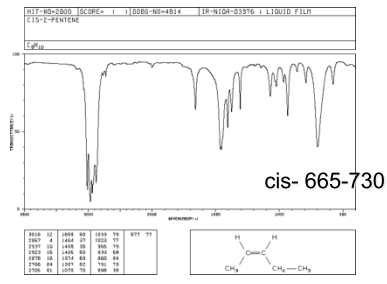




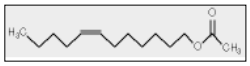


Answer

Is the following IR of cis or trans 2 -pentene? **A) cis 2-pentene**



Chemical Communication: Smell / Pheromones



http://chemconnections.org/COT/COT-chemcomm-eg.html

Pheromone Synthesis
[20:40-23:51]

http://www.learner.org/resources/series61.html

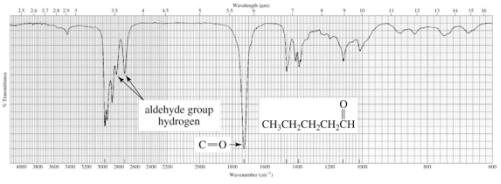
Summary:
C–H bond absorption and hybridization of the carbon atom

IR Absorptions of Carbon–Hydrogen Bonds

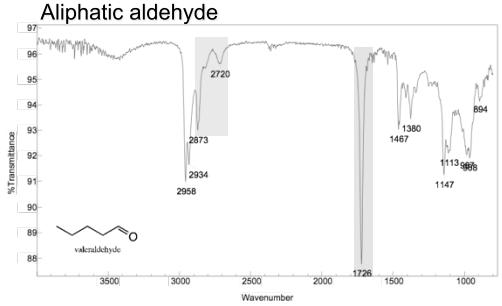
Carbon–Hydrogen Stretching Vibrations	Wavenumber (cm^{-1})
C≡C–H	~3300
C=C–H	3100–3020
C–C–H	2960–2850
R–C(=O)–H	~2820 and ~2720

Carbon–Hydrogen Bending Vibrations		Wavenumber (cm^{-1})
CH_3–, $-CH_2-$, $-\underset{|}{CH}-$		1450–1420
CH_3–		1385–1365
R,H C=C R,H	trans	980–960
R,R C=C H,H	cis	730–675
R,R C=C R,H	trisubstituted	840–800
R,H C=C R,H	terminal alkene	890
R,H C=C H,H	terminal alkene	990 and 910

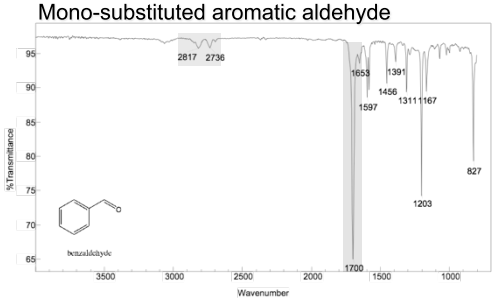
Distinctive Stretch of C–H Bond in an Aldehyde (the "waggle" vibration)



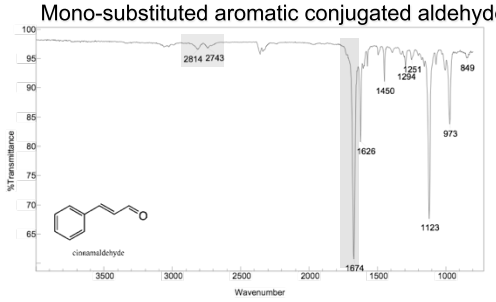
Aliphatic aldehyde



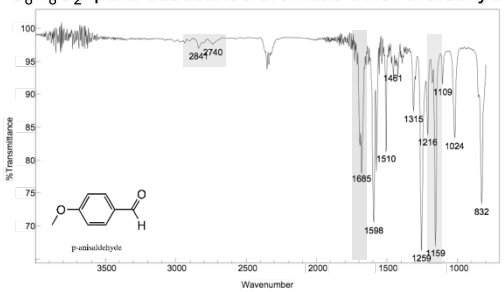
Mono-substituted aromatic aldehyde



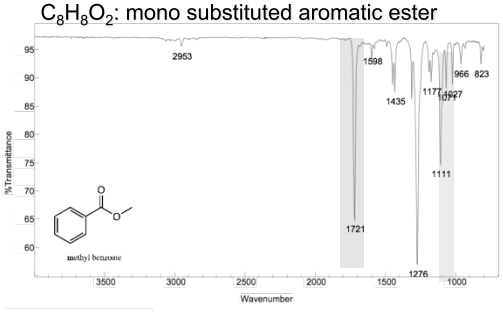
Mono-substituted aromatic conjugated aldehyde



$C_8H_8O_2$: para-substituted aromatic ether & aldehyde



$C_8H_8O_2$: mono substituted aromatic ester



Infrared Spectroscopy

Common Functional Groups

IR Handout

IR Cards

http://chemconnections.org/general/chem121/Spectroscopy/IR-handout-11.htm

Aromatic Absorption Frequencies

Structural unit	Frequency, cm^{-1}
Bending vibrations of derivatives of benzene	
Monosubstituted	730-770 and 690-710
Ortho-disubstituted	735-770
Meta-disubstituted	750-810 and 680-730
Para-disubstituted	790-840