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M.Sc

Chemistry

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Infrared Spectroscopy

IR Spectroscopy

- Used to identify organic compounds
  - IR spectroscopy provides a 100% identification if the spectrum is matched.
  - If not, IR at least provides information about the types of bonds present.
- Easy to use
  - liquids analyzed between salt plates
  - solids in a KBr pellet
  - small amounts of unknowns via an FTIR microscope
  - analysis time typically < 10 minutes
- Inexpensive
  - FTIR spectrophotometers are found in most labs.

IR Spectroscopy

- IR is used to measure the vibrational frequencies of bonds in the molecule.
  - Bonds are not rigid. A bond can be viewed as a spring with a weight at each end.
  - Each bond has a characteristic frequency.
  - The IR scans a range of frequencies (in the infrared part of the electromagnetic spectrum). Any frequency which matches the characteristic frequency of a bond will be absorbed.

IR Spectrophotometers

- In the old days, the frequencies were stepped through, one at a time, and the absorption measured.
  - This means of data collection was very slow.
- Laser technology and computers have made available a much faster means of data collection.

FTIR Spectrophotometers

- **Fourier Transform Infrared Spectrophotometer**
  - **Uses an interferometer and polychromatic light (all frequencies used at one time, instead of one at a time) to generate an interferogram.**
  - **The interferogram is then mathematically decoded by a Fourier transformation.**
    - **interferogram**
      - **intensity vs time**
    - **after the Fourier transformation**
      - **intensity vs frequency…an IR spectrum**

FTIR Spectrophotometers

- http://www.chemistry.oregonstate.edu/courses/ch361-464/ch362/irinstrs.htm
- **FTIR spectrophotometers collect data very quickly and, of course, the spectra can be stored and reviewed electronically.**

An IR Spectrum

- **A plot of % transmittance vs vibrational frequency in wavenumbers $\bar{\upsilon}$ (cm^{-1})**

$c = \lambda\upsilon$

λ = wavelength
υ = frequency
c = speed of light in a vacuum

→ $\frac{1}{\lambda} = \frac{\upsilon}{c}$

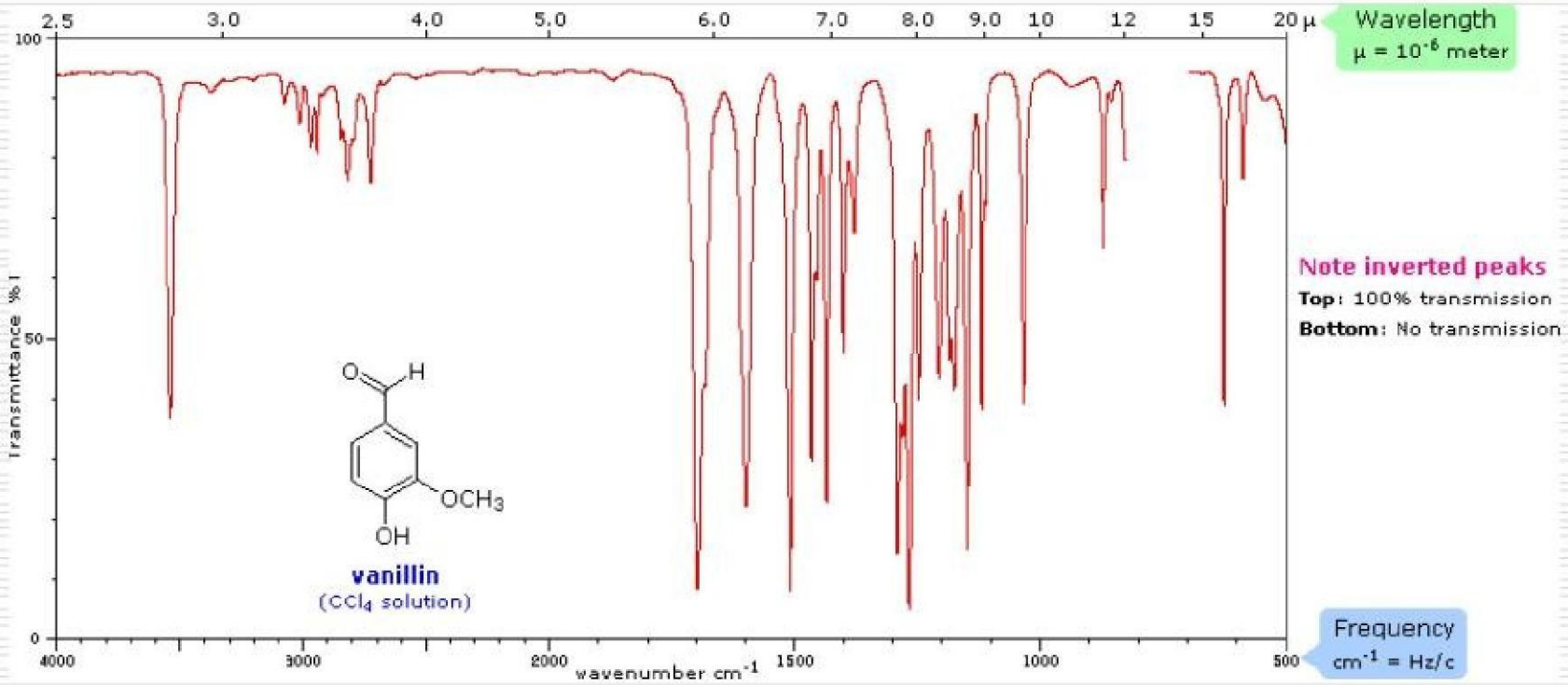
$$\bar{\upsilon} = wavenumber = \frac{1}{\lambda} = \frac{10000}{\lambda(\mu m)}$$

Wavenumbers

- The higher the wavenumber, the shorter the wavelength.

$$\bar{\upsilon} = wavenumber = \frac{1}{\lambda} = \frac{10000}{\lambda(\mu m)}$$

An IR Spectrum



from http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm

An IR Spectrum

- The wavelength of IR radiation is in the 2.5-25 micron range (compare to visible light in the 400-700 nm range).
- The frequencies of IR radiation are more conveniently expressed by a wavenumber $\bar{\upsilon}$ (cycles per cm), than by υ (cycles per 3 x 10^{10} cm).

Characteristic Vibrational Frequencies of Bonds

- Bonds are not rigid but behave like a spring with a mass at either end.
  - Obey Hooke's Law: F = -kx
  - This gives rise to a characteristic frequency for the vibration:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{reduced\_mass}}$$

$$reduced\_mass = \frac{m_1 m_2}{m_1 + m_2}$$

Characteristic Vibrational Frequencies of Bonds

- Characteristic frequency for the vibration:

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{reduced\_mass}}$$

- The frequency is affected by
  - the masses of the atoms in the bond
  - the strength of the bond

Characteristic Vibrational Frequencies of Bonds

- The lower the mass, the higher the vibrational frequency.
  - Stretching frequencies for bonds to carbon: C-H > C-C > C-N > C-O

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{reduced\_mass}}$$

Characteristic Vibrational Frequencies of Bonds

- The stronger the bond, the higher the vibrational frequency.
  - Stretching frequencies
    - C≡C > C=C > C-C
    - C≡N > C=N > C-N
    - C≡O > C=O > C-O
    - spC-H > sp^2C-H > sp^3C-H

$$\upsilon = \frac{1}{2\pi}\sqrt{\frac{k}{reduced\_mass}}$$

Number of Vibrational Frequencies in a Molecule

- There are *3n-6* possible vibrational modes in a nonlinear molecule with no symmetry
  - Symmetry reduces the number of possible vibrational modes.
- Water has 3 possible vibrational modes.
- Formaldehyde has 6.

The Fingerprint Region is Unique to the Molecule

- In addition, the vibration of a particular bond in a molecule affects the whole molecule.
  - The various harmonics of a bond vibration can combine and lead to a number of combinational bands.
    - The intensity of these bands is usually 1/100 the intensity of the main vibrational absorptions.
    - These make up the "fingerprint region." (occur at $<1250\ cm^{-1}$)

Intensity of IR Absorptions

- In order for a vibration mode to absorb in the infrared, the vibrational motion must cause a change in the dipole moment of the bond.
- The intensity of the IR "peaks" is proportional to the change in dipole moment that a bond undergoes during a vibration.
  - C=O bonds absorb strongly.
  - C=C bonds generally absorb much less.

How to Analyze an IR Spectrum

- Pay the most attention to the strongest absorptions:
  - -C=O
  - -OH
  - $-NH_2$
  - $-C\equiv N$
  - $-NO_2$
- Pay more attention to the peaks to the left of the fingerprint region (>1250 cm^{-1}).

How to Analyze an IR Spectrum

- Pay the most attention to the strongest absorptions.
- Pay more attention to the peaks to the left of the fingerprint region (>1250 cm^{-1}).
- Note the absence of certain peaks.
- Be wary of O-H peaks, water is a common contaminant.

Characteristic IR Wavenumbers

Functional group	wavenumber (cm^{-1})
sp^3 C-H str	~2800-3000
sp^2 C-H str	~3000-3100
sp C-H str	~3300
O-H str	~3300 (broad*)
O-H str in COOH	~3000 (broad*)
N-H str	~3300 (broad*)
aldehyde C-H str	~2700, ~2800

***The peak is broad when H bonding is extensive. Otherwise, the peak can be sharp.**

Characteristic IR Wavenumbers

Functional group	wavenumber (cm^{-1})
C=C isolated	~1640-1680
C=C conjugated	~1620-1640
C=C aromatic	~1600
C≡N	just above 2200
C≡C	just below 2200
C=O ester	~1730-1740
C=O aldehyde, ketone, or acid	~1710 (aldehyde can run 1725)
C=O amide	~1640-1680

How to Analyze an IR Spectrum

- Look for what's there and what's not there.
- **C-H absorption**
  - The wavenumber will tell you sp^3(C-C), sp^2(C=C), sp (C≡C) and perhaps aldehyde.
- **Carbonyl (C=O) absorption**
  - Its presence means the compound is an aldehyde, ketone, carboxylic acid, ester, amide, anhydride or acyl halide.
  - Its absence means the compound cannot be any of the carbonyl-containing compounds.

How to Analyze an IR Spectrum

- **O-H or N-H absorption**
  - This indicates either an alcohol, N-H containing amine or amide, or carboxylic acid.
- **C≡C and C≡N absorptions**
  - Be careful: internal triple bonds often do not show up in IR spectra.

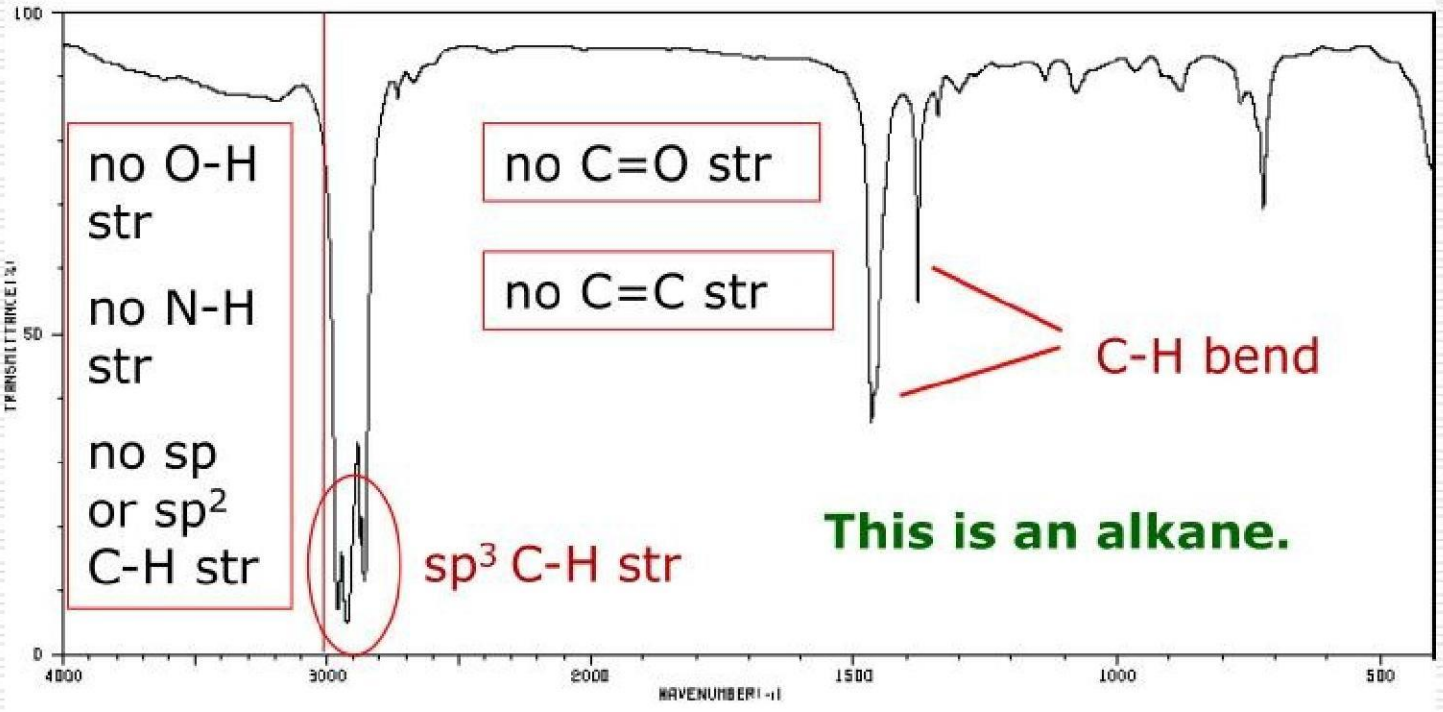
How to Analyze an IR Spectrum

- **C=C absorption**
  - Can indicate whether compound is alkene or aromatic.
- **N-O of NO_2 absorption**
  - This is a distinctive, strong doublet that it pays to know (1515-1560 & 1345-1385 cm^{-1}).

How to Analyze an IR Spectrum

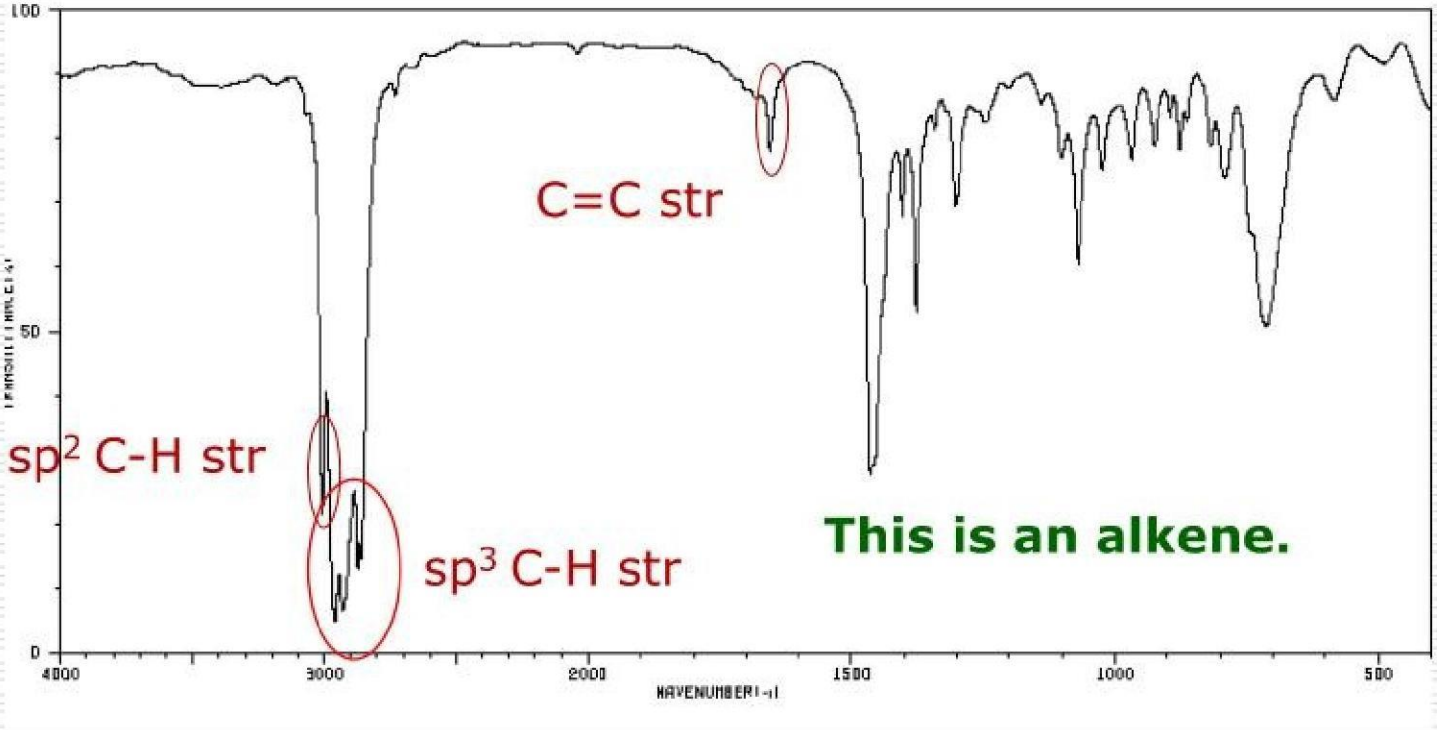
- Read the scale for the value of the wavenumbers (be able to interpolate), or
- Read the wavenumbers in the table provided.

IR Spectra - Examples



SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 10/15/09)

IR Spectra - Examples



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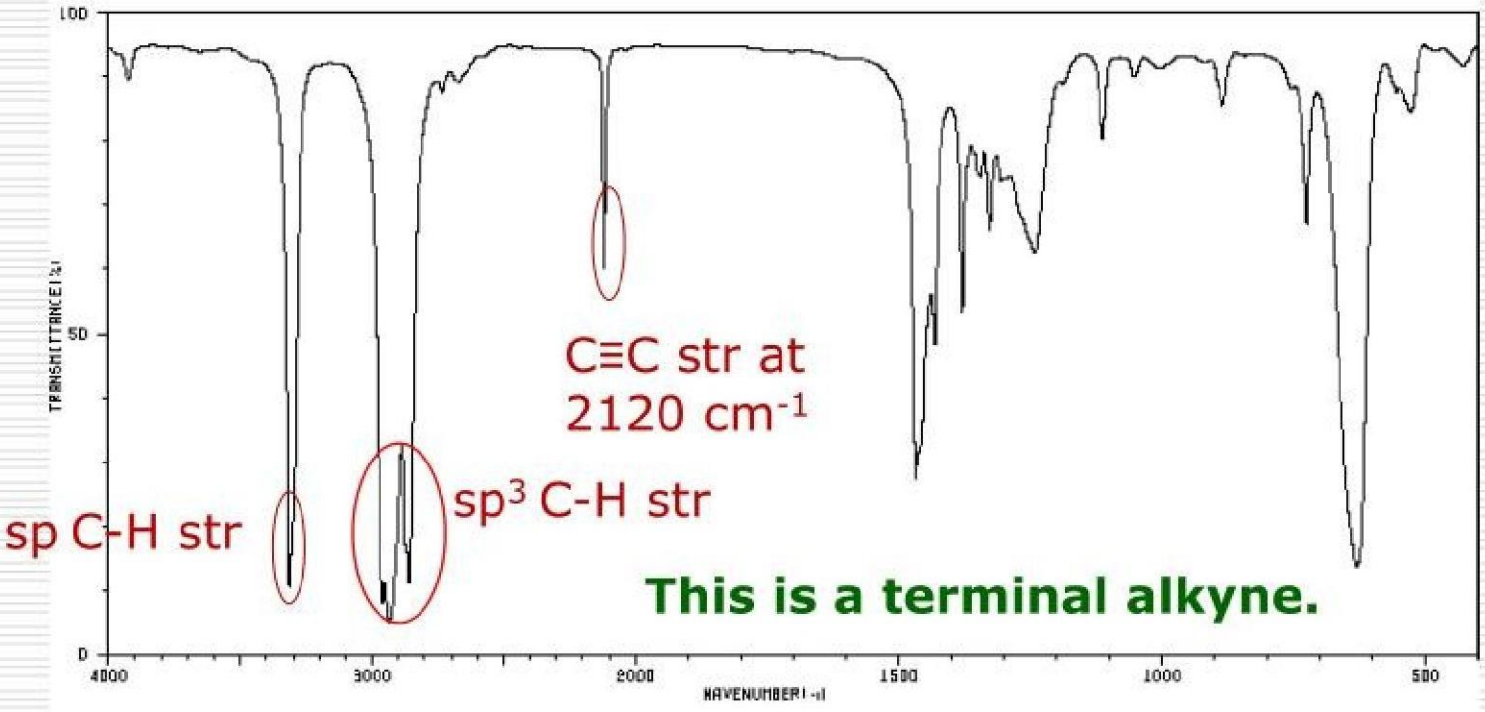
IR Spectra - Examples



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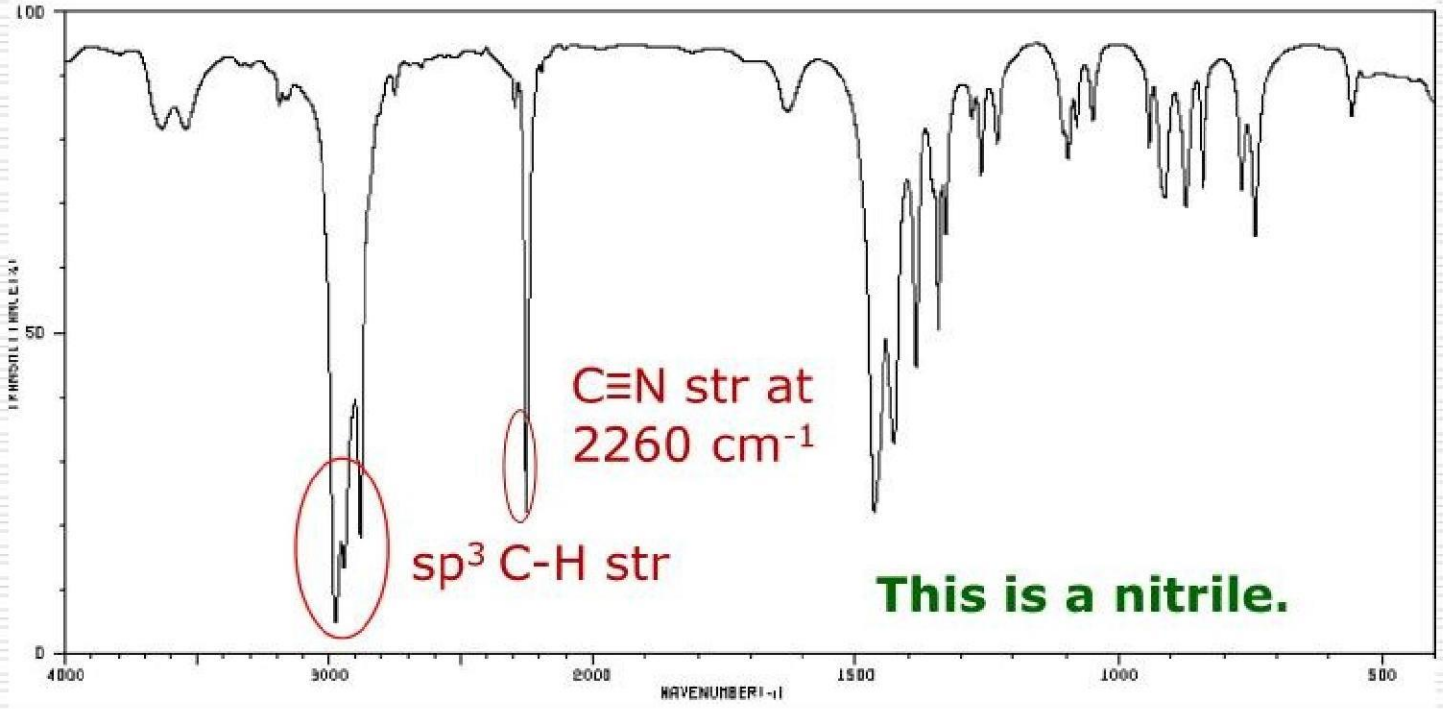

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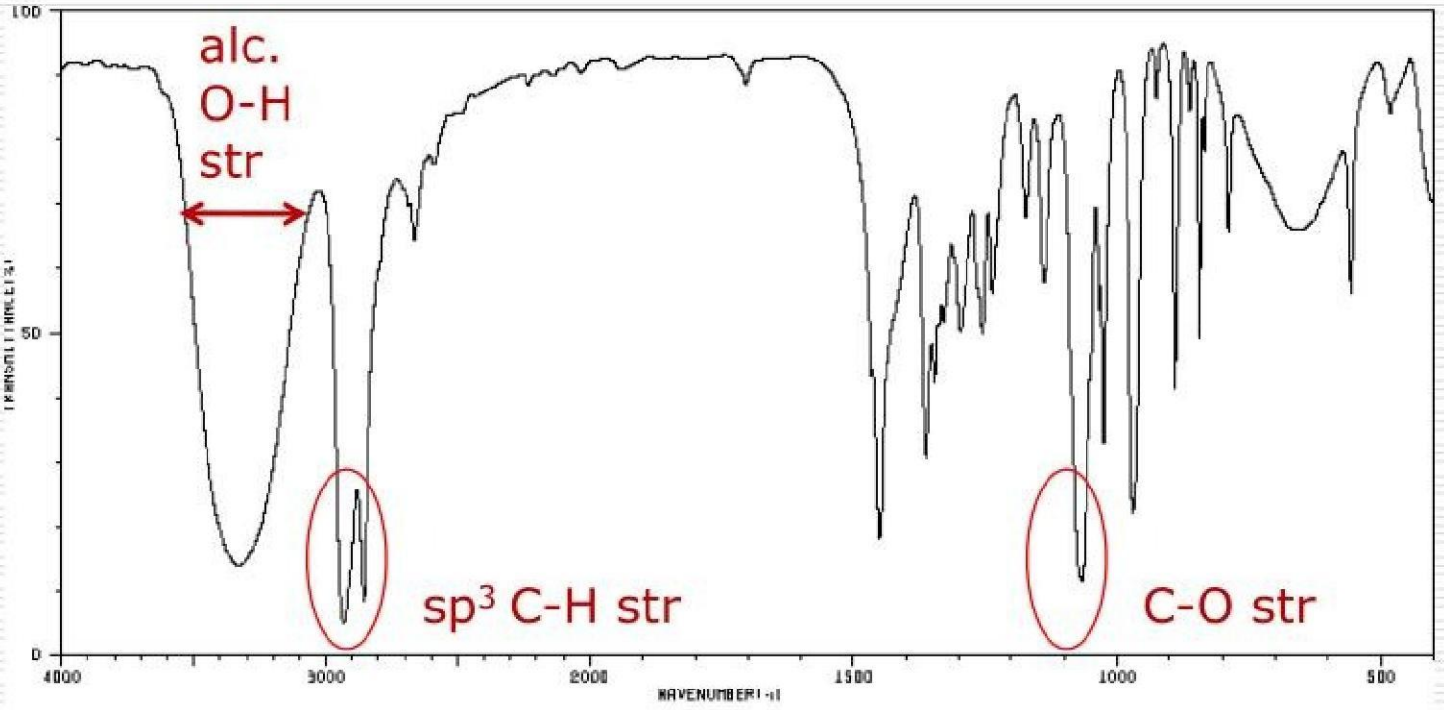


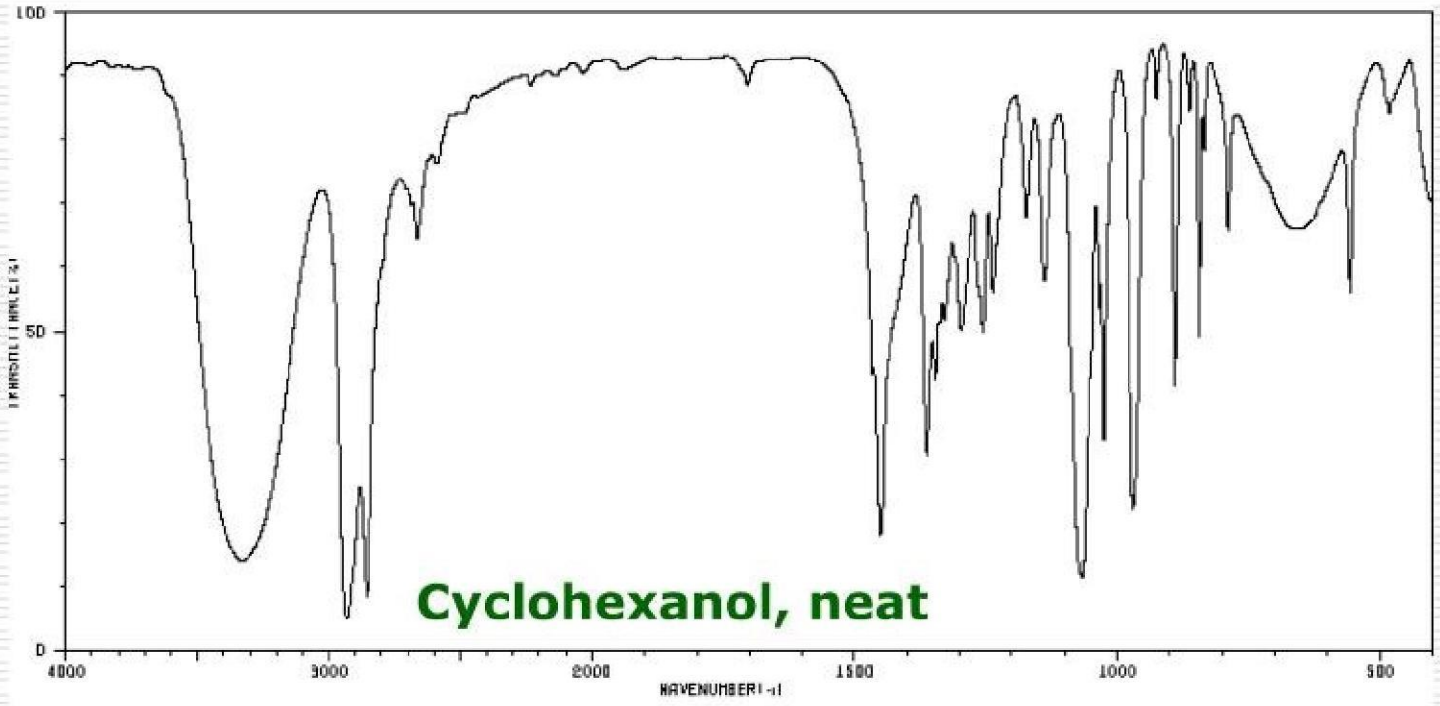
This is an alcohol.

SDBSWeb : http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 10/16/09)

How to Analyze an IR Spectrum

- O-H absorption, peak shape
  - Peak shapes are influenced by hydrogen bonding.
  - Lots of H-bonding, broad peak around 3300 cm^{-1}.
  - In a dilute solution, there is little H bonding and the O-H peak is sharper and around 3500 cm^{-1}.
- This can happen to N-H and the acid O-H as well .

IR Spectra - Examples



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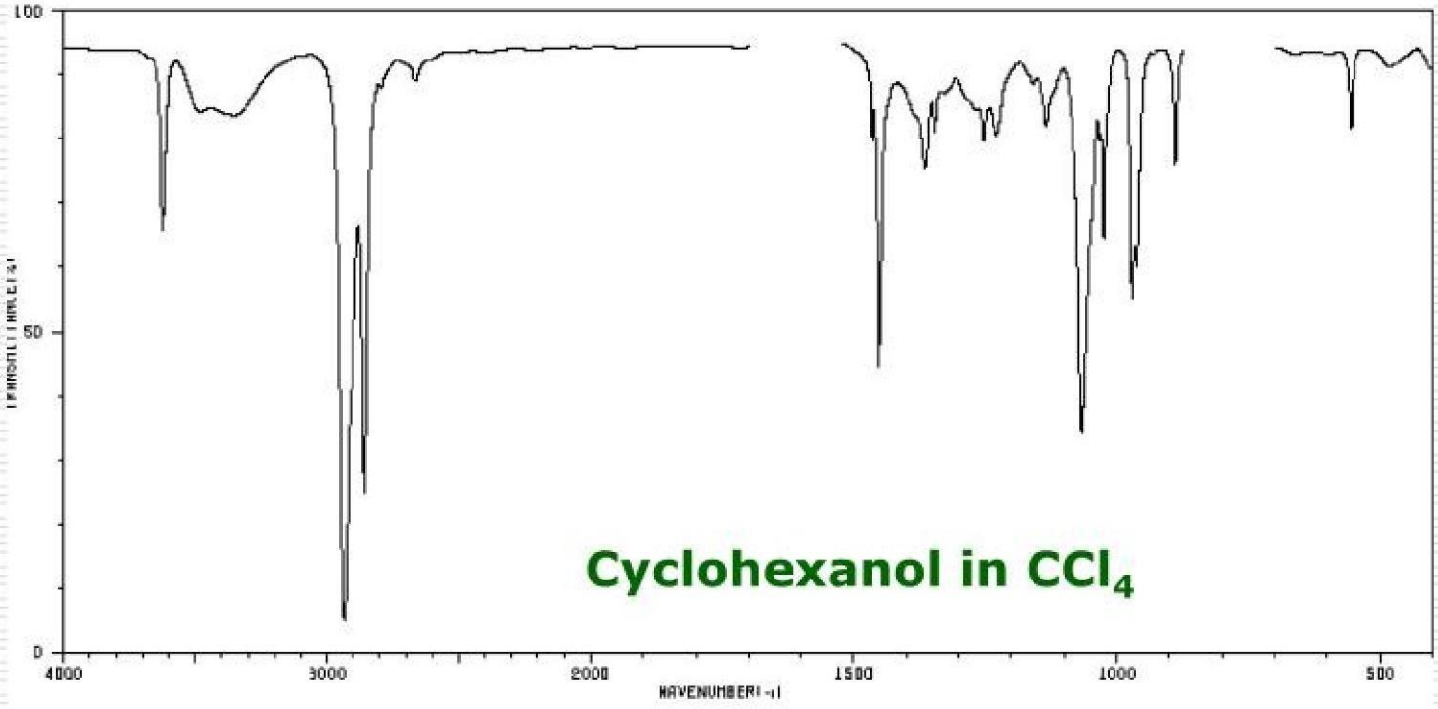

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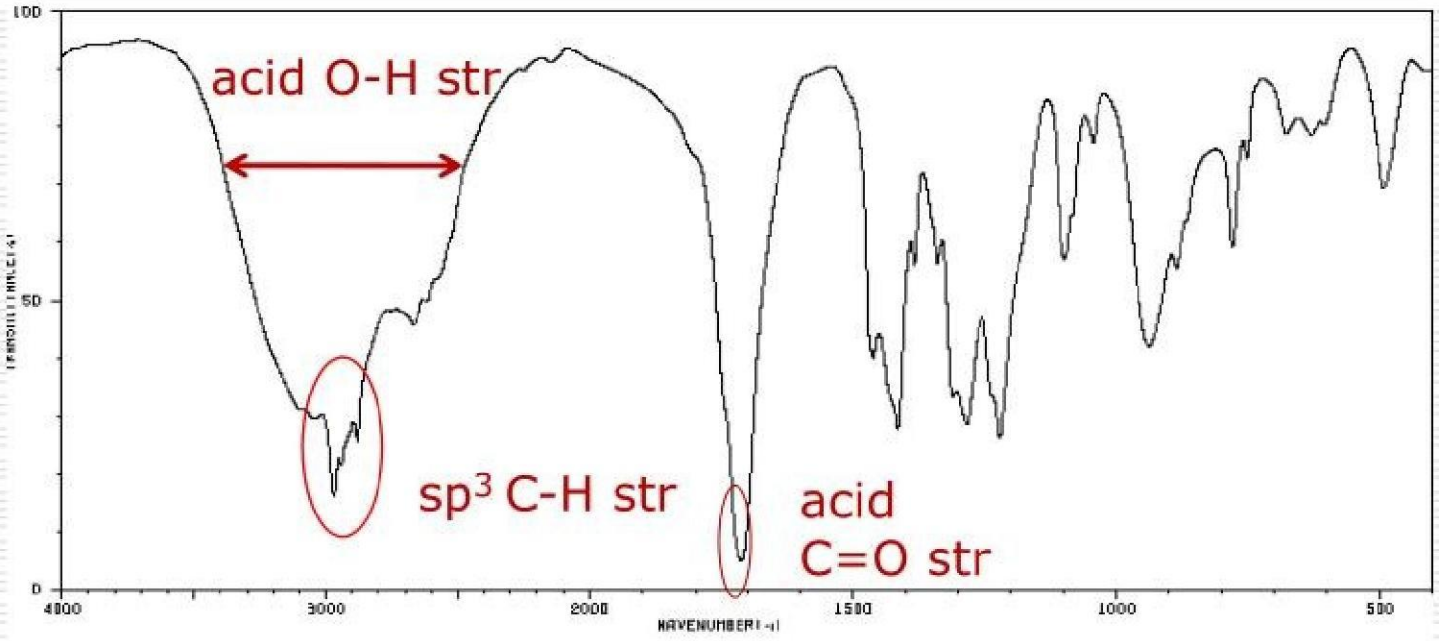
IR Spectra - Examples



This is a carboxylic acid.

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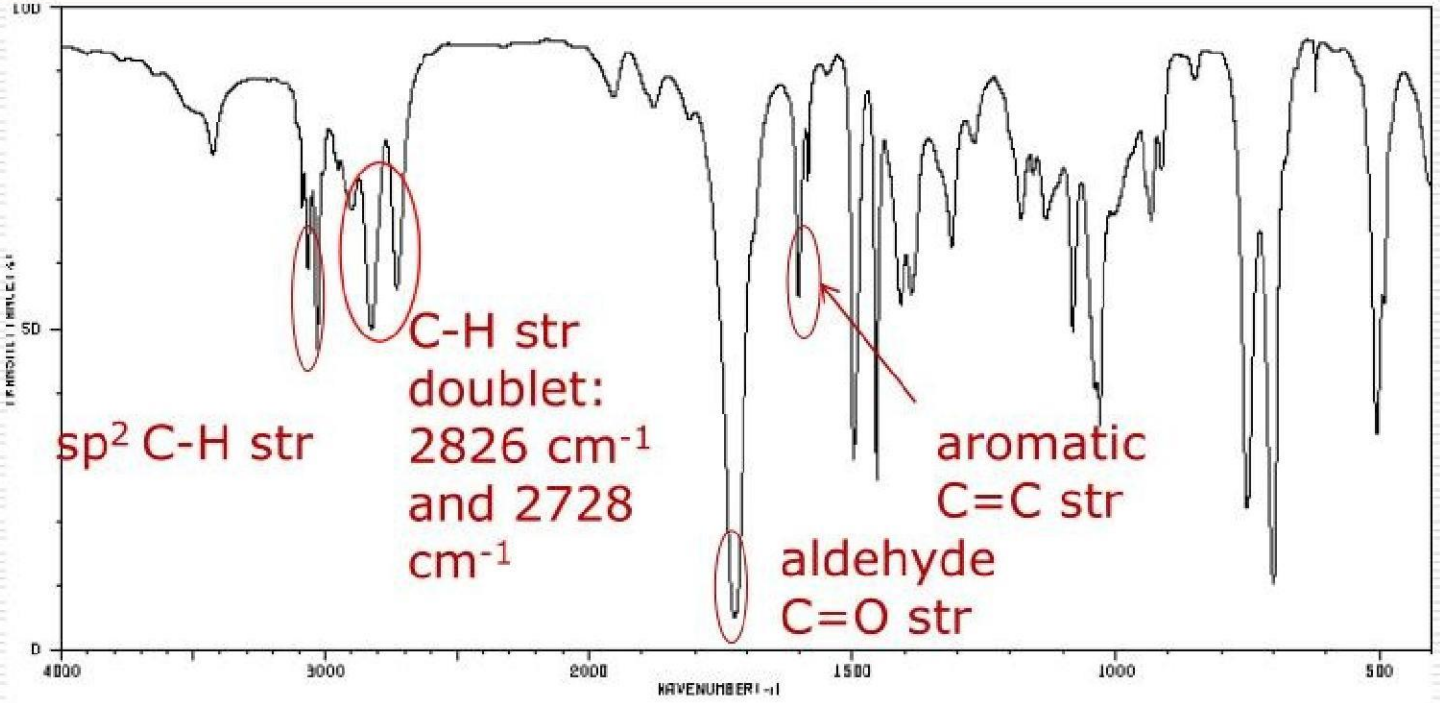
IR Spectra - Examples



This compound has two functional groups: a benzene ring and an aldehyde.

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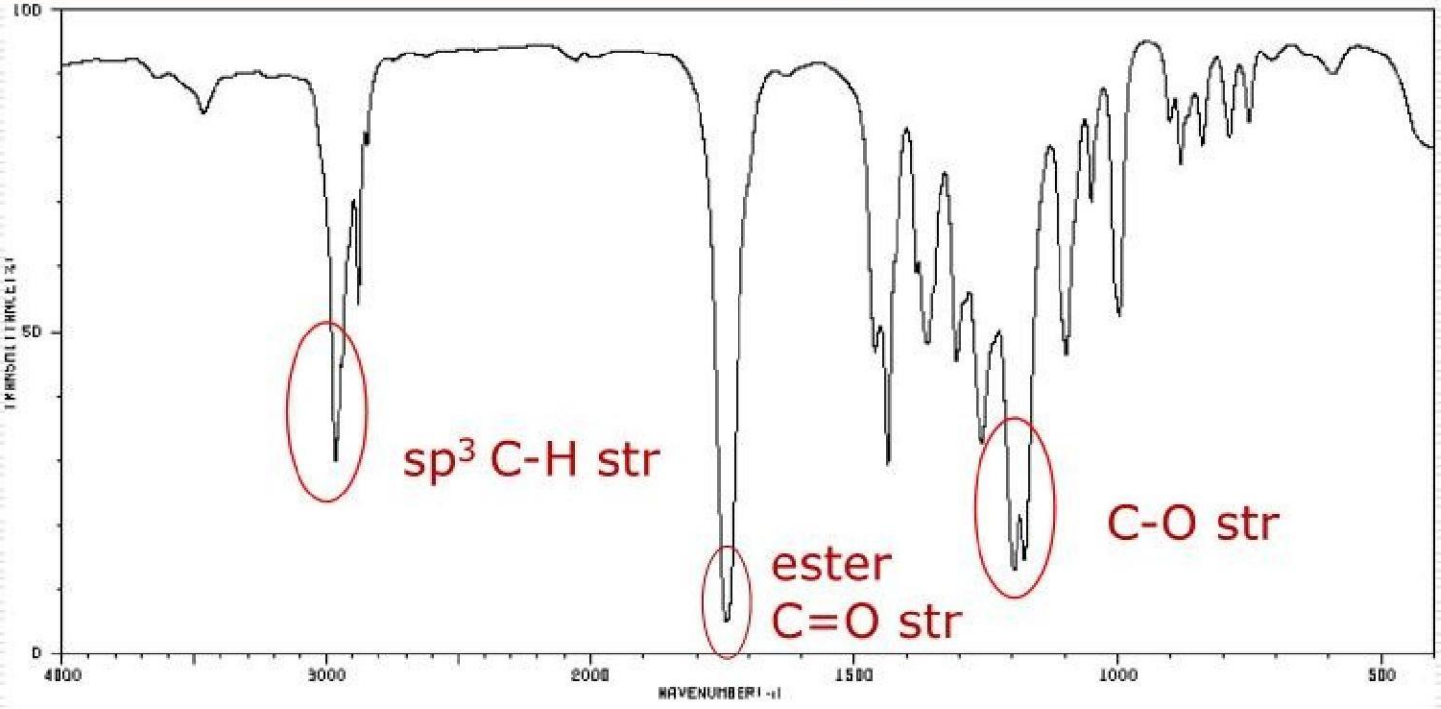
IR Spectra - Examples



This is an alkyl ester. Esters and ketones have fairly similar spectra.

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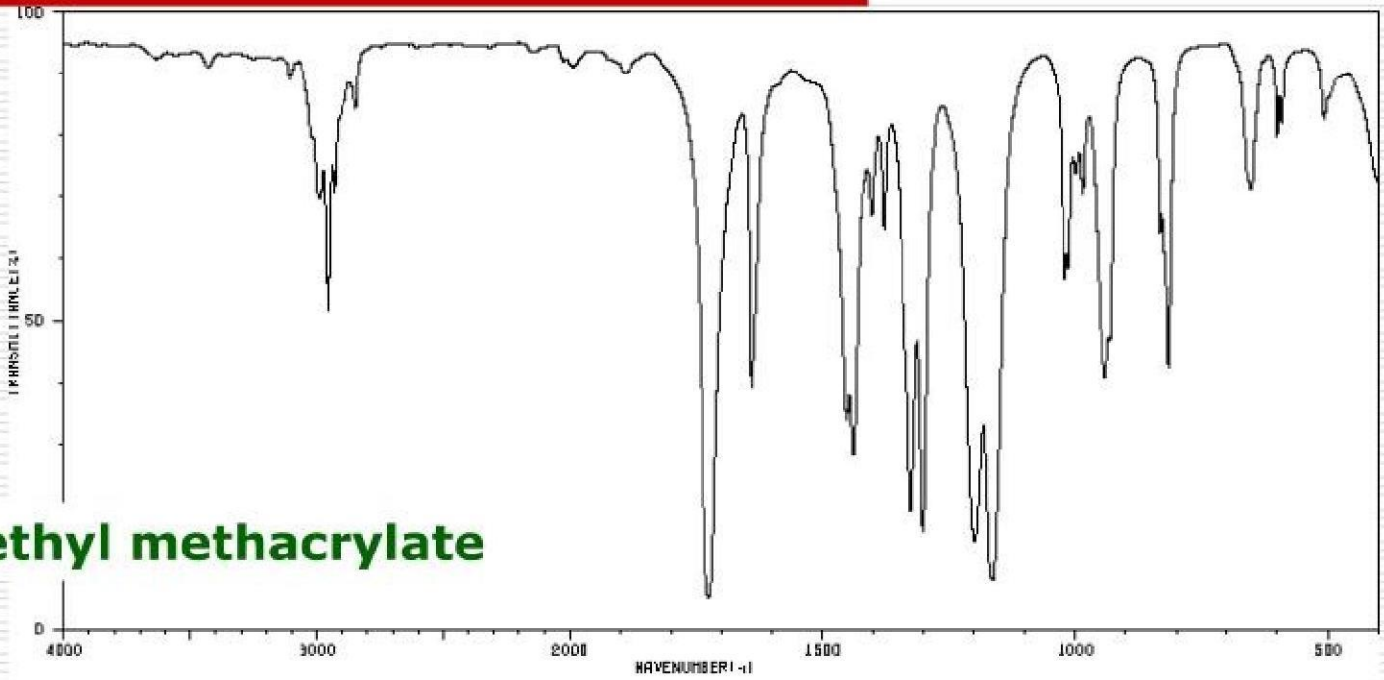
Effects of Conjugation

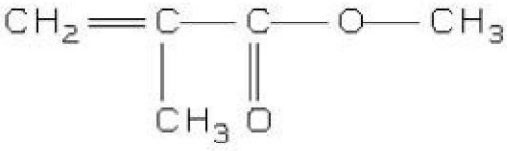
- Conjugation will lower typical absorption frequencies of double bonds due to the presence of some single bond character.
  - C=C
  - C=O
- Ring strain in cyclic compounds goes the other way and increases frequencies.

IR Spectra – Effect of Conjugation



methyl methacrylate

3107	86	1453	32	1164	7	832	62
2987	66	1440	26	1021	55	816	41
2955	50	1403	64	1014	57	653	68
2931	68	1378	62	999	70	601	77
2848	81	1326	18	985	68	592	79
1726	4	1302	15	942	39	508	79
1639	37	1200	19	931	44	502	81



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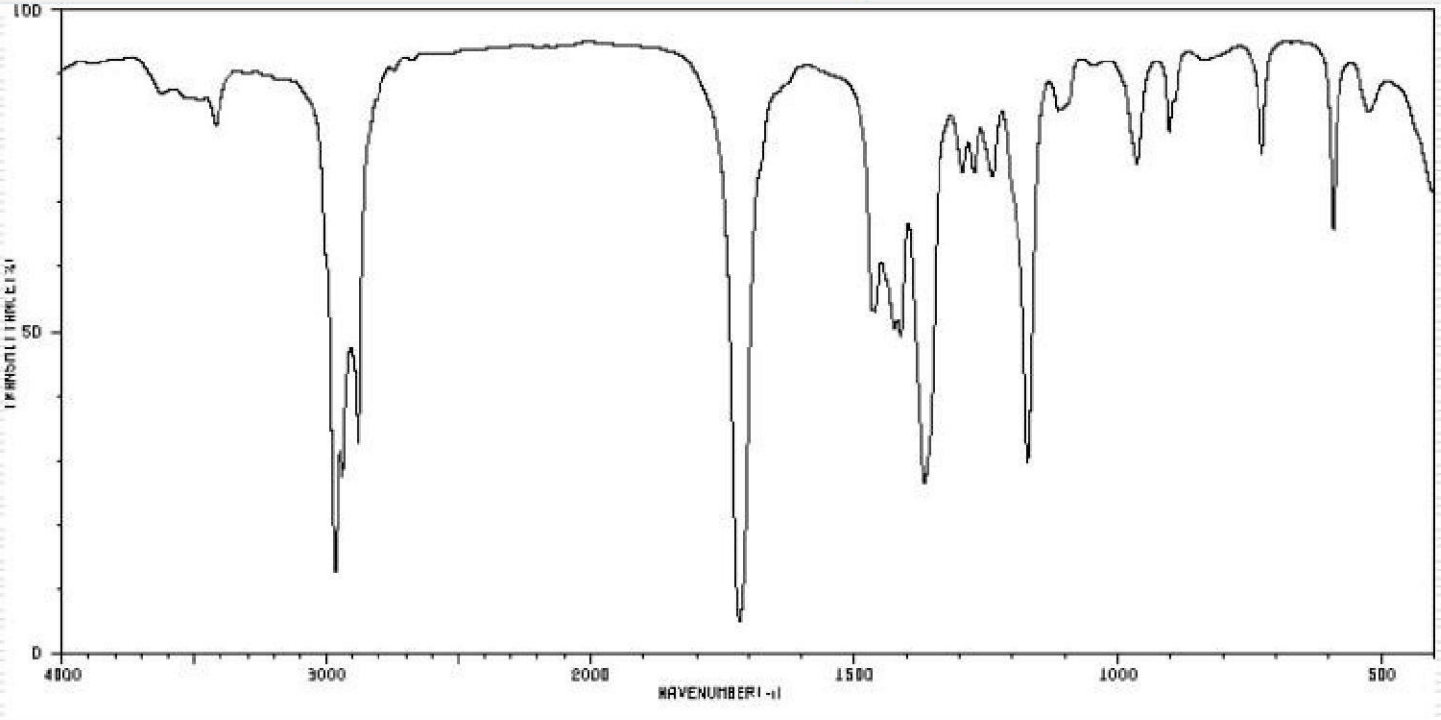

What functional group(s) is (are) present?

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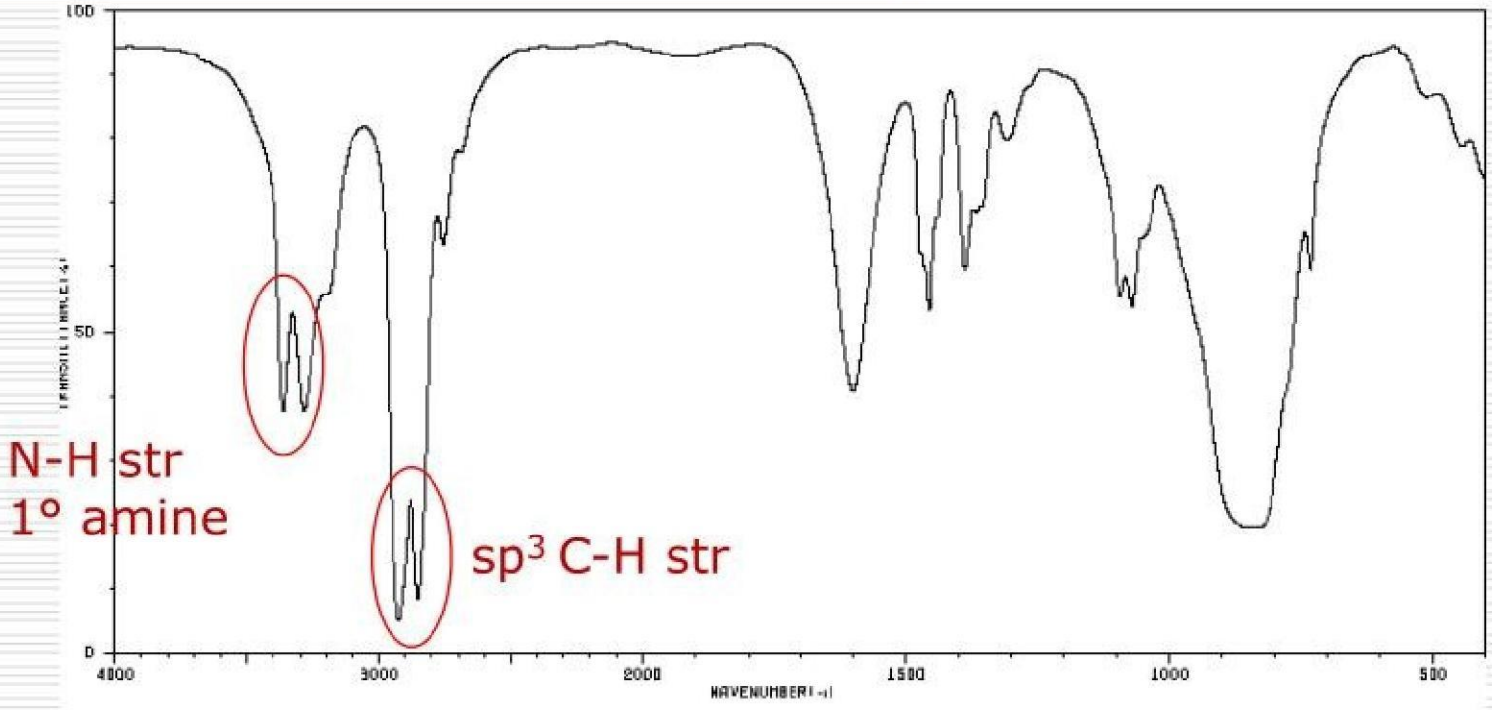
IR Spectra - Examples



This is a primary alkyl amine.

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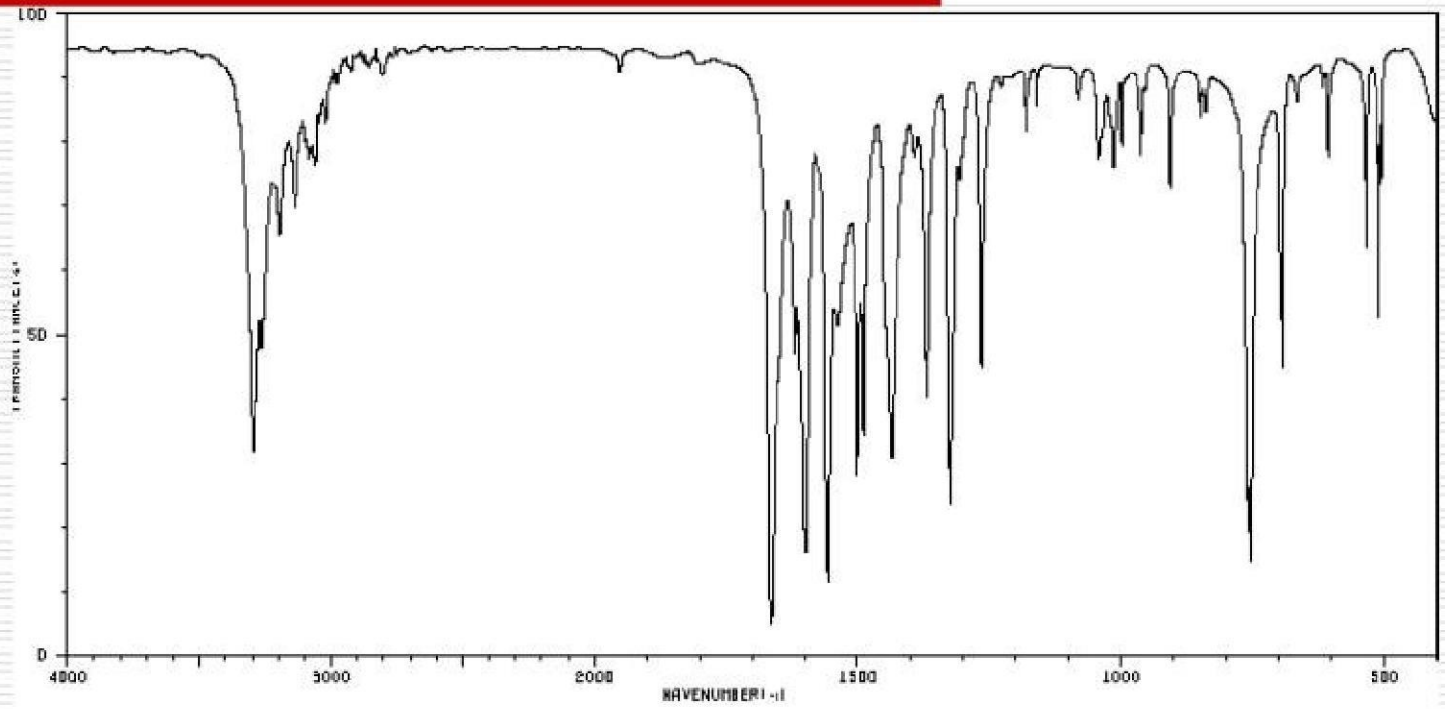
IR Spectra - Examples



3294	30	3022	79	1489	33	1180	79	761	23
3261	46	1665	4	1436	29	1042	74	754	13
3196	82	1620	44	1393	74	1014	72	694	45
3137	66	1599	16	1369	38	999	77	607	74
3083	74	1557	10	1324	22	962	74	534	60
3059	74	1538	49	1307	72	908	70	511	50
3045	79	1501	28	1265	43	768	62	506	70

Identify all major absorptions and functional groups. (acetanilide)

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How to Analyze an IR Spectrum

- http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/InfraRed/infrared.htm
- **Nothing takes the place of sitting down with actual spectra and studying them.**