Infra-red Spectroscopy

Molecular vibrations are associated with the absorption of energy (infrared activity) by the molecule as *sets of atoms* (molecular moieties) vibrate about the mean center of *their* chemical bonds.

The infrared spectrum is a plot of the extent of absorption of electromagnetic radiation at frequencies that correlate to the vibration of the aforementioned specific sets of chemical bonds/atoms in a molecule.

There is a fundamental requirement for the presence infrared activity; there must be a *net change in dipole moment* during the vibration of the moiety of the molecule.

Observed IR frequencies of a molecule can be attributed to,

a. normal (fundamental) modes of vibration
b. combination modes of vibration
c. overtones
d. Fermi resonance - coupling of fundamental modes with overtone or combination bands.
e. Vibrational and rotational couplings' (rotational fine structure).

Normal (Fundamental) Modes

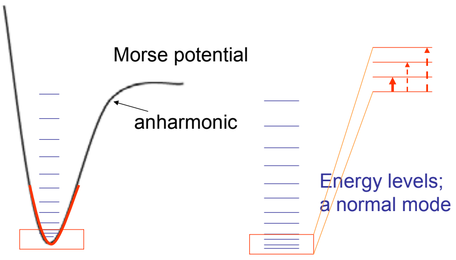
A normal mode is a motion in the molecule where a ‘set of atoms’ move as a sinusoid with a specific frequency.

Number of normal modes of vibration for a given molecule with N atoms is 3N – 6 (nonlinear), 3N – 5 (linear) of which (N-1) are stretching vibrations and the rest are deformations.

The basic model for a normal mode of vibration is a simple harmonic oscillator. Modified harmonic oscillator would describe the anharmonicity of vibrations.

Simple harmonic oscillator model leads to the Hooke’s law that enables the calculation of the fundamental vibrational frequencies of a molecular ensemble.

Electronic ground state of diatomic is described by the Morse potential. The bottom of which is parabolic is the region where Hooke’s Law is applicable (SHM).



$$E_v = \left(v + \frac{1}{2}\right)h\nu$$

$$v = 0, 1, 2, \ldots; \quad \Delta v = \pm 1$$

Classical mechanical expression for the natural (fundamental) stretching frequency of masses m_1 and m_2 joined by a spring of force constant k, from Hooke’s Law (for each normal mode);

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}} \qquad \text{where,} \quad \mu = \frac{m_1 m_2}{m_1 + m_2}$$

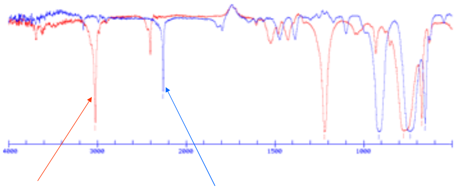
k = force constant

c = velocity of light

ν = fundamental vibrational frequency

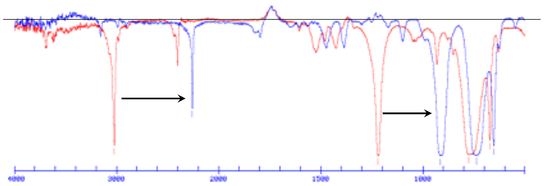
Vibrations of some small molecules

The Effects of Mass on Frequency



chloroform and deuterochloroform

http://www.chem.ucla.edu/~webspectra/irintro.html



Mode of vibration	$CHCl_3$	$CDCl_3$
C-H stretching	3020	2256
C-H bending	1219	912
C-Cl stretching	773	737
C-Cl bending	671	652

Hydrogen Bonding

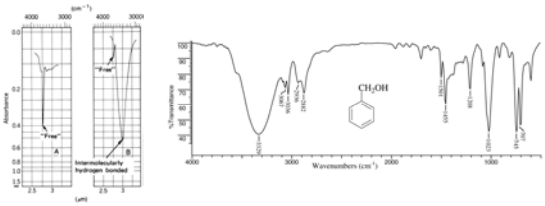
$X^{-\delta}$ - $H^{+\delta}$.... :Y both X and Y electronegative.

X = carboxyl, hydroxyl, amine, amide
Y = O, N, X, C=C (pi)

H-bond alters the force constant of participating groups;
X-H lowers frequency, increase intensity and broaden bands.

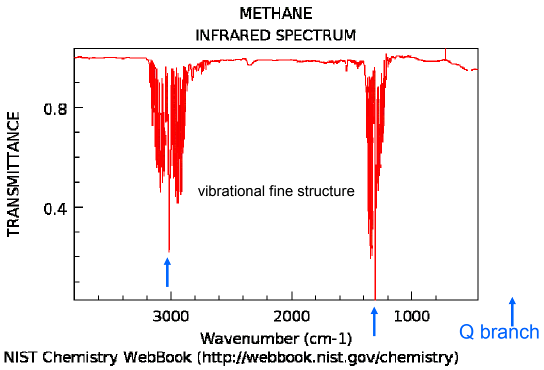
C=C lowers frequency to a lesser degree.

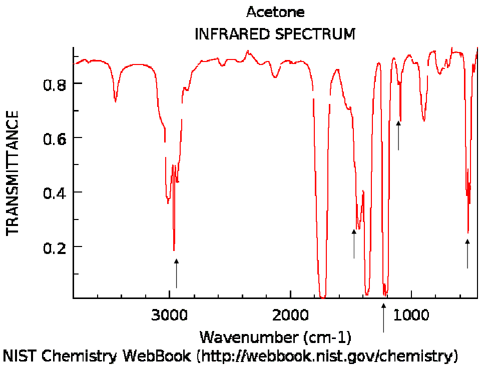
Intra-molecular H-bonding is temperature dependent, concentration independent. Be mindful of the possible solute/solvent interactions.



In reality, the number observed frequencies in the spectrum is less than 3N-5 or 3N-6. The reasons for the smaller than expected number are; several of the vibrations are have close frequencies, some redundant and some degenerate, that is, the same amount of energy is required for these vibrations.

On the other hand, especially in gas phase and/or at higher spectral resolutions although a small number of vibrational modes is predicted a more complex spectra is observed. This is because at relatively high resolution, the *rotational fine structure* originating from rotational bands are observable.



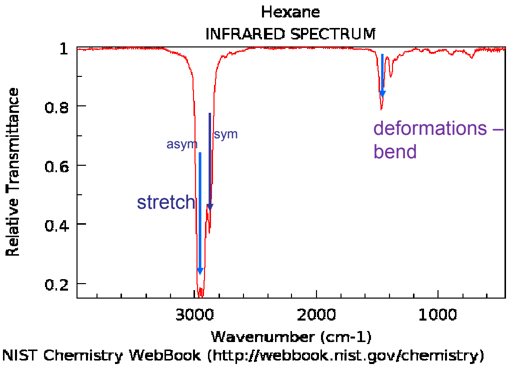


Group frequencies of different molecules featuring the same *functional group* are generally close in most compounds.

The group frequencies are useful to characterize a compound.

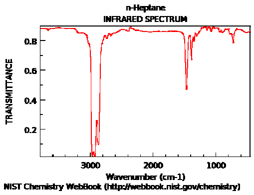
Combination of group frequencies and the skeletal frequencies of IR spectrum identify a specific compound uniquely. This uniqueness forms the basis of the use of reference spectra for spectral matching, visually or computer-based (searching), for the identification of ‘unknowns’ from their infrared spectrum.

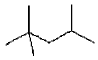
Observed absorption frequencies in the infrared spectrum are from the simple harmonic vibrations of sets of atoms.

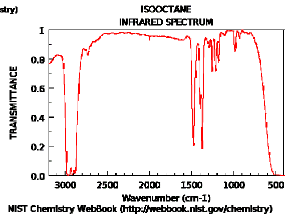


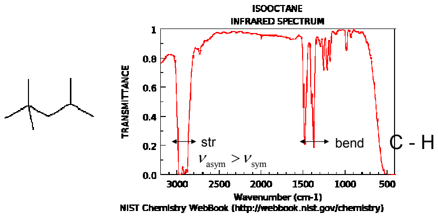
(group frequencies of aliphatics; methyl and methylene)

A given absorption band assigned to a functional group *increases proportionately with the number times that functional group occurs within the molecule.*

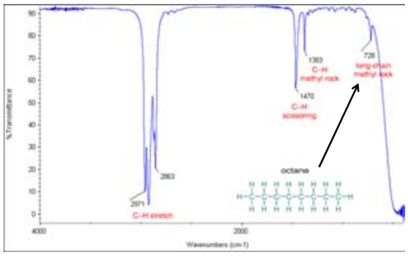








Also present in the spectrum are various other deformation motions (angular changes), such as bending and twisting about certain centers within a molecule, etc. also contribute to the overall absorption spectrum (low frequency).



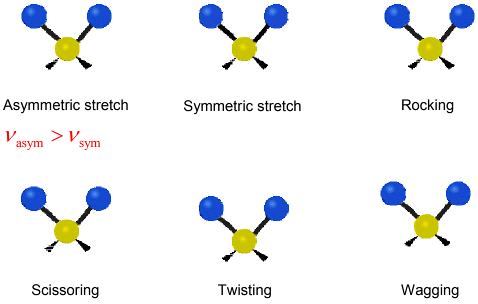
There are other spatially related scenarios e.g. in-plane and out-of-plane vibrations, the differences between cis and trans spatial relationships. A variety of multi-centered vibrations that are defined as twisting or rocking modes exist.

Many of these are exhibited with the C-H vibrations that occur in saturated, unsaturated and aromatic compounds.

Molecular moieties of the type AB_2 (methylene, amine, etc.) generate two stretching absorptions due to symmetric and asymmetric stretching motions, if isolated A-B, $\nu_{A\text{-}B}$, then for the AB_2 moiety;

$$\nu_{asym} > \nu_{A\text{-}B} > \nu_{sym}$$

Bending and stretching vibrational modes for the **CH_2 group**



http://www.chemistry.ccsu.edu/glagovich/teaching/316/ir/vibration.html

Molecular symmetry of the static or the dynamic (during vibration) molecule has a large impact on the spectrum, in addition to factors such as relative electronegativity, bond order and relative mass of the participating atoms.

Transitions to higher energy levels (forbidden) can occur - *overtone bands*; with approximately twice the fundamental frequency (first overtone) and second (thrice the fundamental) and third (four times fundamental). Sometimes these higher frequencies (very low intensity) are observed in NIR spectral regions.

Also seen are *combination bands* (sum and difference), due to transitions from energy states higher than the ground state (hot bands) and bands due to interactions between a weaker overtone or combination band and a fundamental of the same or similar frequency, known as Fermi resonance bands.

In Fermi bands two relatively strong absorptions are observed, where normally only a single absorption is expected for the fundamental.

As functional groups are added to the backbone, additional bands are observed, which are associated with the fundamental vibrations of the functional groups, or indirectly related to interactions between functional groups and the basic structure.

Some interactions can result in a change in the appearance of the spectrum, e.g. hydrogen bonding (solvent effects).

backbone

↓ functional groups

molecule

Deduce the fundamental backbone or the parent hydrocarbon structure *whenever possible*.

For most molecules (organic) the backbone is a hydrocarbon, with linear carbon chains, branched chains and cyclic structures (aliphatic/aromatic) with functional groups attached to it. The infrared spectrum can provide information on the existence or absence of most of these functional groups either directly or inferentially.

It would also provide information specific to the group itself, and also on the interaction of the group with other parts of the molecule and on the spatial properties of the group, such as conjugation, location and orientation of double bonds (cis/trans, medial/terminal or pendant).

Vibrational Group Frequencies

Interpretation of spectra is accomplished by recognizing the characteristic *strengths, shapes and patterns of IR absorptions, and matching to published vibrational group frequency* data to that of the spectrum (frequency tables).

Note and familiarize with the general appearances of group frequencies.

Interpretation is based not only on the *presence* of particular bands within the spectrum, but also the *absence* of bands.

Entire classes of compounds can be excluded as possible candidates because of the absence of bands.

A very characteristic group of compounds, from a spectral point of view, are the multiple-bonded nitrogen compounds, such as cyanides and cyanates. These typically have characteristic absorptions, which are easy to assign, and *are free from spectral interferences*.

The same behavior seen for some of the hydrides of heteroatoms, such as sulfides (thiols), silanes, and phosphines.

Hydrocarbons and Molecular Backbone

For aliphatic and aromatic structures the spectral contributions are characterized, by C-H vibrations (stretching, bending etc).

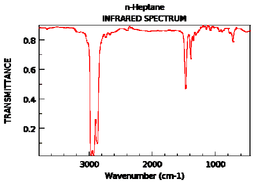
In the case of aromatic compounds, ring C=C-C stretching and bending vibrations; for the alkenes and alkynes multiple bonding vibrations are highly characteristic and diagnostic.

Saturated Aliphatic and Alicyclic Compounds

The C-H stretch just less than 3000cm^{-1} for methyl and methylene are the most characteristic for recognizing the compound as organic compound containing at least one aliphatic fragment.

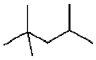
Other characteristics are bending methylene/methyl bands 1470 cm^{-1} and a weak methyl band 1380 cm^{-1}.

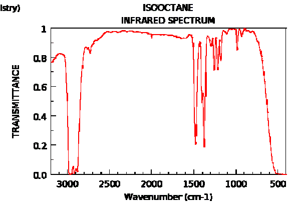
A band at 725–720 cm^{-1} (methylene rocking) is indicative of a long-chain (n >3) linear aliphatic structure.


n-Heptane
INFRARED SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Branching changes the relative size of bands.




ISOOCTANE
INFRARED SPECTRUM

NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

Unsaturated Compounds

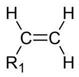
Bands between 3150 - 3000 cm^{-1} are almost exclusively indicative of unsaturation; alkene C-H and/or aromatic C-H.

For alkene, C=C, terminal (2 bands), pendant and medial double bonds are distinguishable.

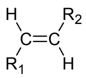
C=C-H, C-H vibrations are useful in distinguishing terminal pendant moieties and also cis /trans compounds.

A fully substituted, medial C=C has only the C=C as the sole indicator of the presence of the double bond, unless the bond is conjugated with a second unsaturated site (indirect info.).

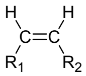
Unsaturated Compounds; alkenes



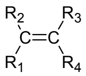
terminal
vinyl



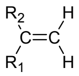
trans



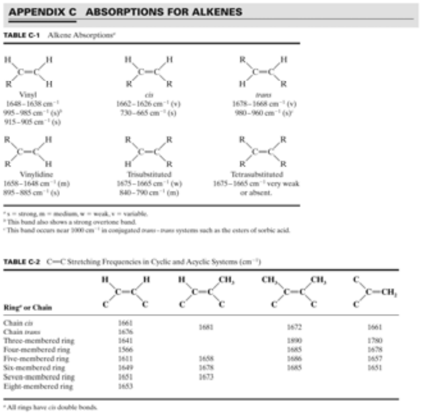
cis



medial alkene
fully substituted



pendant alkene
vinylidene



APPENDIX C ABSORPTIONS FOR ALKENES

TABLE C-1 Alkene Absorptions[a]

Vinyl 1648–1638 cm^{-1} 995–985 cm^{-1} (s)[b] 915–905 cm^{-1} (s)	*cis* 1662–1626 cm^{-1} (v) 730–665 cm^{-1} (s)	*trans* 1678–1668 cm^{-1} (v) 980–960 cm^{-1} (s)[c]
Vinylidine 1658–1648 cm^{-1} (m) 895–885 cm^{-1} (s)	Trisubstituted 1675–1665 cm^{-1} (w) 840–790 cm^{-1} (m)	Tetrasubstituted 1675–1665 cm^{-1} very weak or absent.

[a] s = strong, m = medium, w = weak, v = variable.
[b] This band also shows a strong overtone band.
[c] This band occurs near 1000 cm^{-1} in conjugated *trans*-*trans* systems such as the esters of sorbic acid.

TABLE C-2 C=C Stretching Frequencies in Cyclic and Acyclic Systems (cm^{-1})

Ring[a] or Chain				
Chain *cis*	1661	1681	1672	1661
Chain *trans*	1676			
Three-membered ring	1641		1890	1780
Four-membered ring	1566		1685	1678
Five-membered ring	1611	1658	1686	1657
Six-membered ring	1649	1678	1685	1651
Seven-membered ring	1651	1673		
Eight-membered ring	1653			

[a] All rings have *cis* double bonds.

Aromatic Compounds

The existence of aromatic rings in a structure is normally determined from the C-H and C=C-H ring-related vibrations. The C-H str. Occurs above 3000 cm^{-1} and is typically as a multiplicity of weak-to-moderate bands, (compared with the aliphatic C-H str.)

C-H out-of-plane bending vibrations 1000-650 cm^{-1}, are used to determine the degree and nature of substitution on the ring. No absorption in 1000-650 cm^{-1} – no unsat C-H.

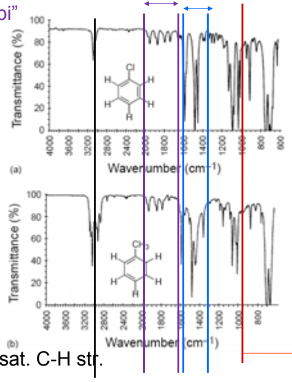
Aromatic combination bands 2000-1660 cm^{-1}.

Aromatic ring vibrations 1600-1300cm^{-1} (pair), position and ratio of bands depend on the nature of substituents.

Aromatic skeletal vibrations

“Combi”

in-plane C-H bending



out-of plane C-H bend 1000-650

Unsat. C-H str.

Acetylenic Compounds

The spectrum associated with the triple bond structure is characteristic and is influenced by whether the group is terminal or medial.

The H of the terminal acetylene itself is very characteristic.

C≡C	2140–2100	Terminal alkyne (monosubstituted)
C≡C	2260–2190	Medial alkyne (disubstituted)
C–H	3320–3310	Alkyne C–H stretch
C–H	680–610	Alkyne C–H bend
C–H	630 (typical)	Alkyne C–H bend

Functional Groups

F, Cl, Br, I, OH, OR (R=alkyl), NH2, =NH, ≡N

Halogenated Compounds

If single halogen is present the assignment is straightforward.

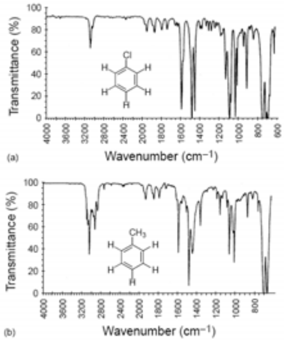
If more than one halogen are present the interpretation is complex, depends on the location of halogens. Halogens are on the same or different carbon atoms, and, if on different atoms then their proximity. Spectral complexity arises from the *restricted rotation* about the carbon–carbon bond leading to specific conformations, with each conformation generates its own contribution to the overall spectrum.

The high electro-negativity of the halogen has a significant impact on the spectrum of neighboring group frequencies.

In such cases, significant shifting of the C-H frequencies can occur and the shift being dependent on the location of the C-H. The halogen enhances or decrease the electron density from the C-H bond shifting to higher frequency and lower frequency, respectively.

Similar effects occur in halogen carrying carbonyl compounds.

On aromatic rings their effect is manifested indirectly from its electronic impact on the in-plane C-H bending vibrations.
In the case of a halogen-substituted ring, the intensity of these vibrations is enhanced relative to other absorptions.

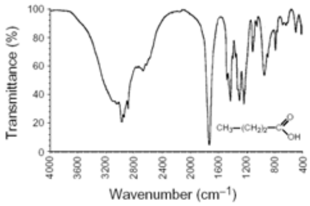


Alcohols, Phenols and Ethers

The -OH functional a dominant and characteristic absorption of all IR frequencies. In most cases –OH group does not exist in isolation, and a high degree of association via H-bonding to other -OH groups occur, intra-molecularly or Inter-molecularly.

The result produces significant band broadening and shift to lower the mean absorption frequency depending on the degree and strength of the H-bonding.

In compounds such as carboxylic acids, with very strong H-bonding forming a stable dimers, a highly characteristic and large shift to lower frequencies is observed.



Note: O-H shape.

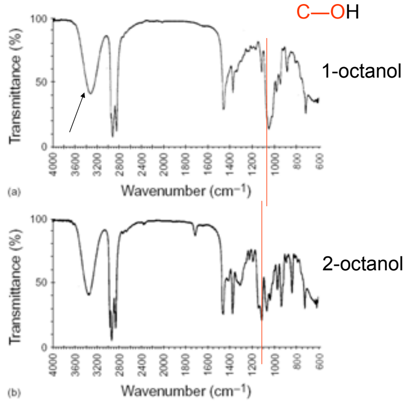
Hydrogen bonded dimers; lowered O-H frequencies.

Alcohols exist as primary, secondary and tertiary. In these cases the C-O str. and out of plane O-H bends and wags frequencies allows differentiation.

Alcohols, Phenols and Ethers

Relationships that exist for the C-O component of the alcohol carry over to the corresponding ether. The main difference is the presence of bonds to C atoms on both sides of the oxygen. Infrared spectroscopy can differentiating these ether bonds, especially when the structures are mixed aliphatic or aliphatic/aromatic.

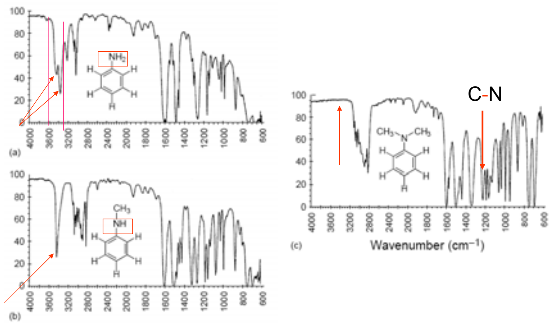
Look for C-O-C.



Amines

IR is very diagnostic, and it is possible to differentiate functional groups primary, secondary (associated with N-H bonds), and tertiary amines (from C-N) bonds.

An important exception is the –NH(CH_3) and –N(CH_3)$_2$ group, which like its counterpart (-OCH_3 in ethers) has a characteristic C-H str. Lower frequency at lower than normal C-H frequency for methyl (Table 1).



N–H stretch 3400-3250 cm-1

- 1° amine: two bands from 3400-3300 and 3330-3250 cm^{-1}
- 2° amine: one band from 3350-3310 cm^{-1}
- 3° amine: no bands in this region

N–H bend (1°, 2° amine only) from 1650-1580 cm^{-1}
C–N stretch (aromatic amines) from 1335-1250 cm^{-1}
C–N stretch (aliphatic amines) from 1250–1020 cm^{-1}
N–H wag (1°, 2° amines only) from 910-665 cm^{-1}

The Carbonyl Group

The carbonyl absorption is almost always one of the most characteristic in the entire spectrum, and it is also most likely to be the most intense spectral feature.

A ketone is considered the *root* compound, with an aldehyde being a special case (carbonyl group – terminal and has one substituent). All of the other carbonyl compounds, can be considered to be derived from the base ketone structure.

The absorption frequency is dependent on the electronic characteristics of the substituents. Spatial and structural factors can be important, in particular ring stress, as in the case of lactones (cyclic esters) and lactams (cyclic amides). The greater the ring stress, the higher is the carbonyl absorption frequency.

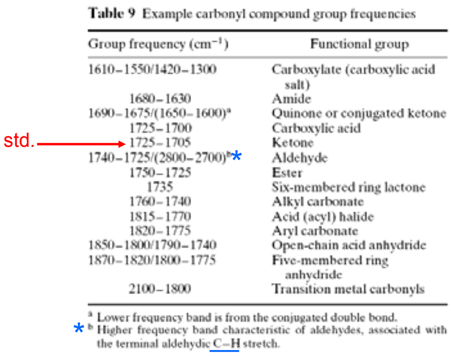


Table 9 Example carbonyl compound group frequencies

Group frequency (cm^{-1})	Functional group
1610–1550/1420–1300	Carboxylate (carboxylic acid salt)
1680–1630	Amide
1690–1675/(1650–1600)[a]	Quinone or conjugated ketone
1725–1700	Carboxylic acid
std. → 1725–1705	Ketone
1740–1725/(2800–2700)[b] *	Aldehyde
1750–1725	Ester
1735	Six-membered ring lactone
1760–1740	Alkyl carbonate
1815–1770	Acid (acyl) halide
1820–1775	Aryl carbonate
1850–1800/1790–1740	Open-chain acid anhydride
1870–1820/1800–1775	Five-membered ring anhydride
2100–1800	Transition metal carbonyls

[a] Lower frequency band is from the conjugated double bond.
* [b] Higher frequency band characteristic of aldehydes, associated with the terminal aldehydic <u>C–H</u> stretch.

Spectral information from the other components of the functional groups are used for the characterization, e.g. carboxylic acids C-O, C-O-H and O-H; esters C-O-C; amides C-N, N-H.

Multiple-bonded and Cumulated Double-bonded Nitrogen Compounds

Hetero-oxy Compounds

Thiols and Thio-substituted Compounds

Spectral Interpretation

an approach

General observations:

The spectral features (absorptions - weak, medium, strong, sharp, broad) are characteristic of certain classes or compounds and/or functional groups. Such features are very helpful in the interpretation process. e.g. the overall appearance of the H-bonded -OH functionality, patterns associated with unsaturation and aromaticity, and the combinations bands of different carbonyl compounds.

A simple spectrum is usually associated with a simple molecular structure. Multiple functionality might reflect a complex structure or that the sample is a mixture.

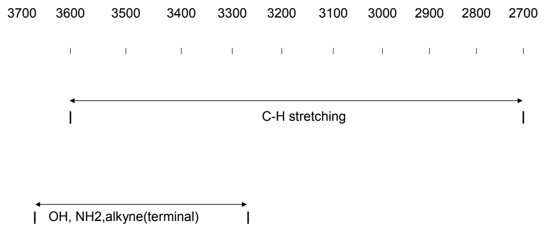
Be mindful about of the existence of spectral coincidences.

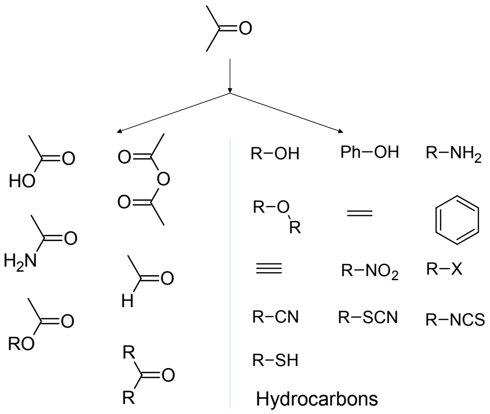
The use of known relative band intensities for certain functional groups can also be helpful in determining whether band overlap is occurring, and in particular to determine whether the bands from a group are being obscured by other more intense bands e.g. overlap of the cis- C-H out-of-plane bending vibration, which is typically overlapped by the -$(CH_2)_n$- rocking.

Incorporate all known chemical and physical information, relevant test data, if available, such as color (highly conjugated compounds and nitro compounds), odor (esters, ketones, unsaturation, and nitro groups, have highly characteristic fragrances or odors), crystalline character, chemical tests.

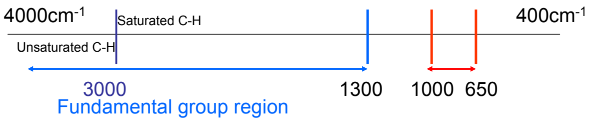
Negative information (no-band regions) is extremely important, because it eliminates major classes compounds as potential candidates reducing the number of possibilities in the interpretation.

Electronic effects such as inductive effect and resonance phenomenon, steric effects H-bonding and ring strain changes the character of isolated bonds and therefore the frequency of absorptions peaks gets modified. Further changes may occur depending on the solvent.





Starting point



Carbonyl, 1760-1690cm^{-1} (present)

O–H (b) 3400-2400	carboxylic acid
C–O (s) band 1300-1000	ester
Doublet ~1810, 1760	anhydride
C–H band (w) 2850,2750	aldehyde
N–H 3400 (m), double	amide
none of the above	ketone

exact position of the carbonyl ⇒ type of carbonyl compound
Table 9

Carbonyl, 1760-1690cm^{-1} (absent)

O–H (broad) + C-O (1300-1000) phenol/alcohol

C–O str.	ether
C=C str.	alkene
aromatic	aromatic
C≡C	alkyne
-NO_2	nitro

Single/double, sharp; 2°/1° N–H band (m) 3400-3250 cm^{-1}

Also examine 900-650 cm^{-1} for aromatics. Also alkyl halides, carboxylic acids, amines, and amides (bending vibrations)….

C=C (w) 1650 double bonds
aromatic (m-s) 1600-1450

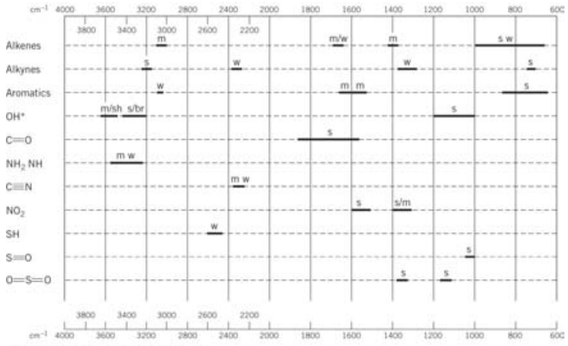
C≡N (m, sharp) 2250
C≡C (w, sharp) 2150
C-H 3300 acetylenic

NO_2 (s) 1600-1539 and 1390-1300

No major functional group bands 4000-1300 cm-1 other than C–H stretches ⇒ **hydrocarbon**

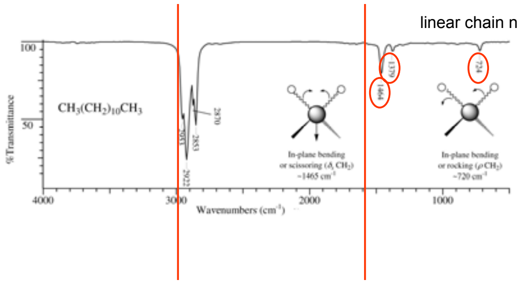
Familiarize with the characteristics of absorption peaks such as weak, medium, strong, sharp, broad etc as you study IR spectra.

After a preliminary examination of the IR spectrum and coming to a tentative conclusion, use data from other spectral sources employ extensive IR tables (e.g. Appendix B) to confirm the structure.



*Free OH, medium and sharp; bonded OH, strong and broad

linear chain n ≥ 3



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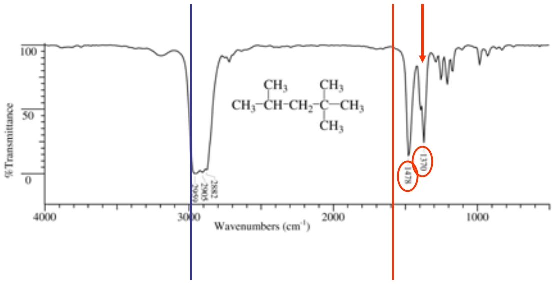

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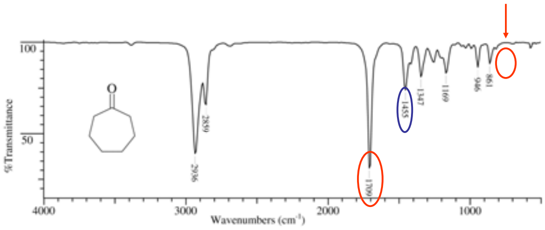

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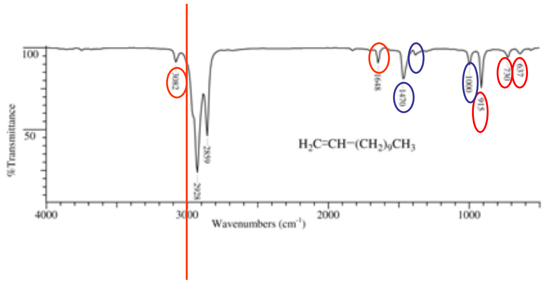

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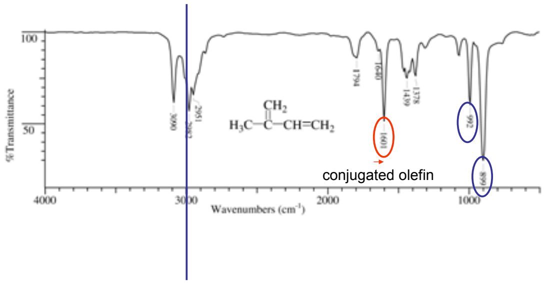

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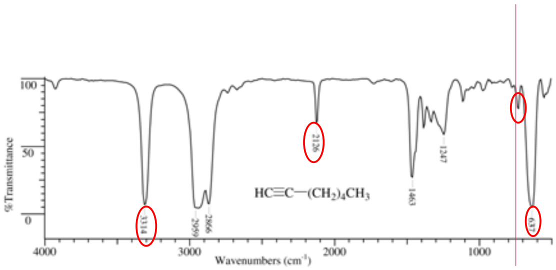

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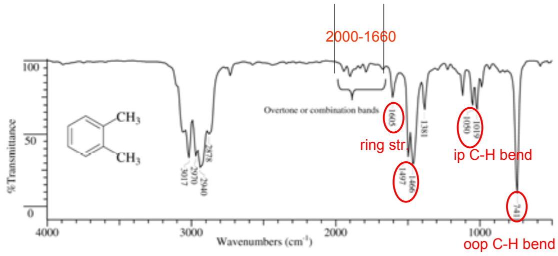

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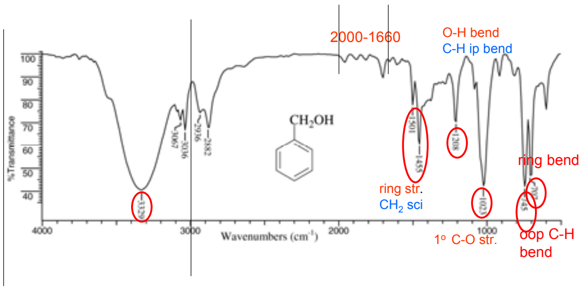

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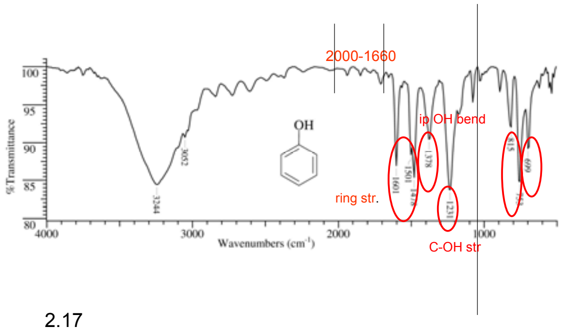

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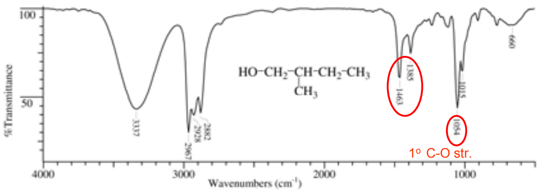

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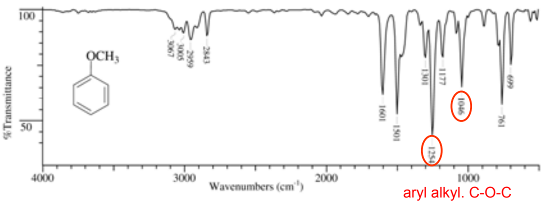

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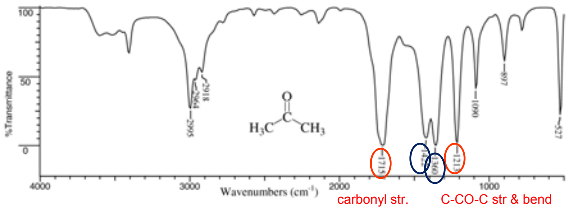

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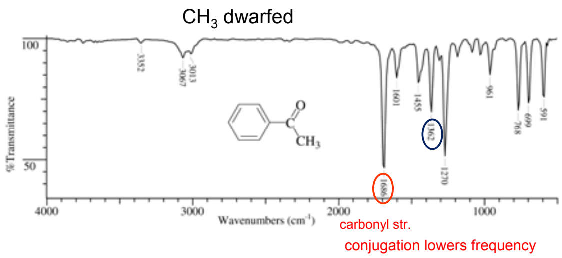

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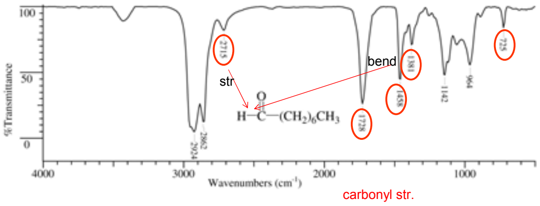

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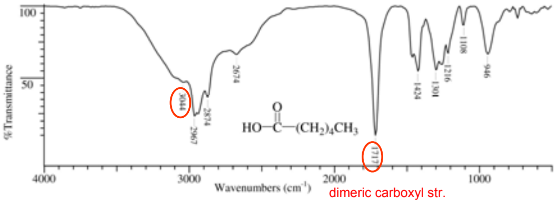

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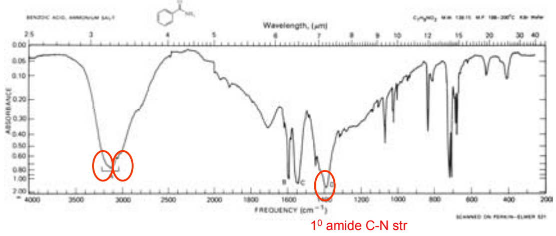

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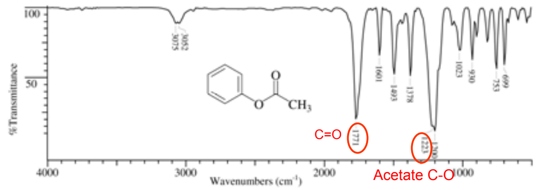

Normal ester 1740

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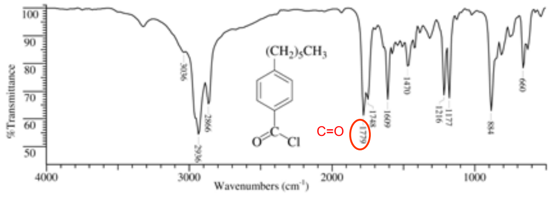

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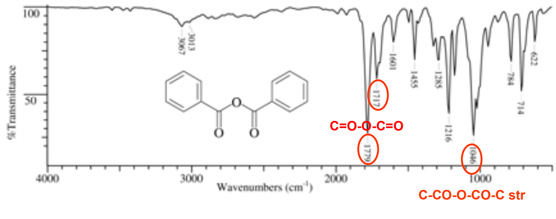

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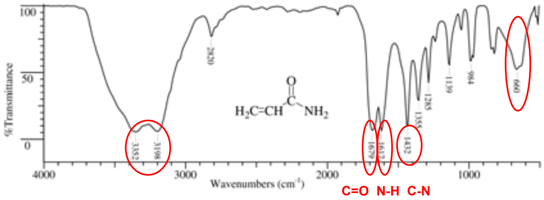

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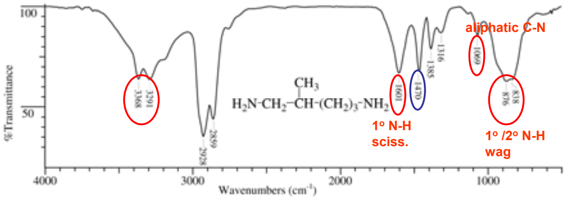

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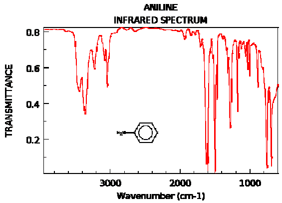

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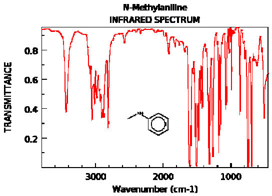

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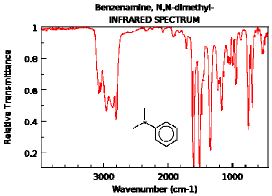

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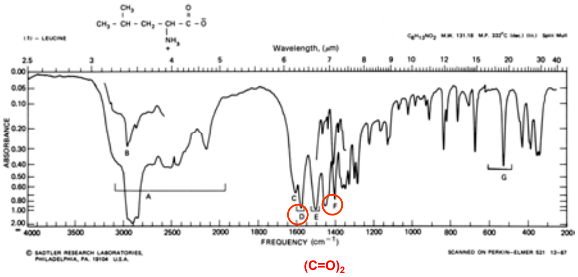

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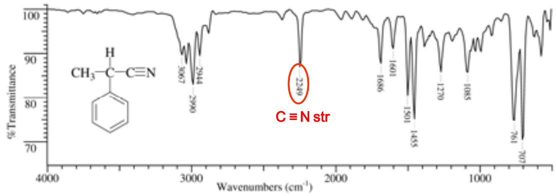

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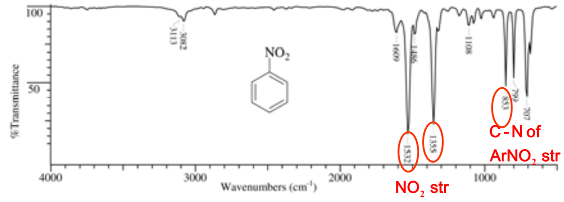

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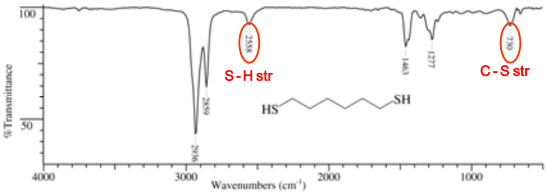

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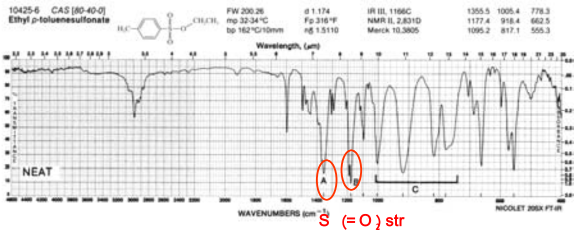

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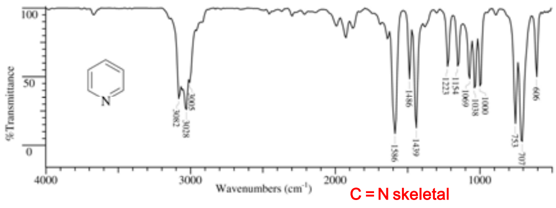

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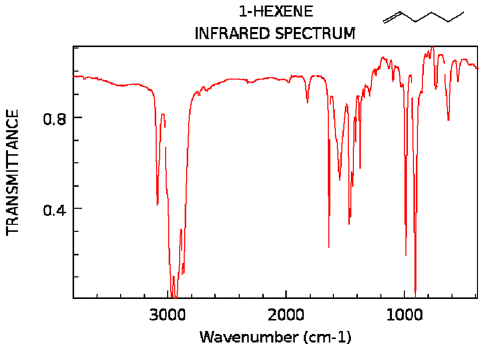

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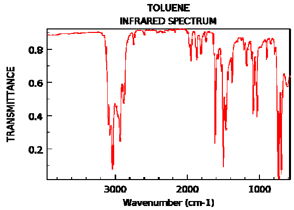

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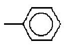

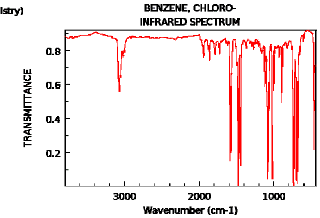

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