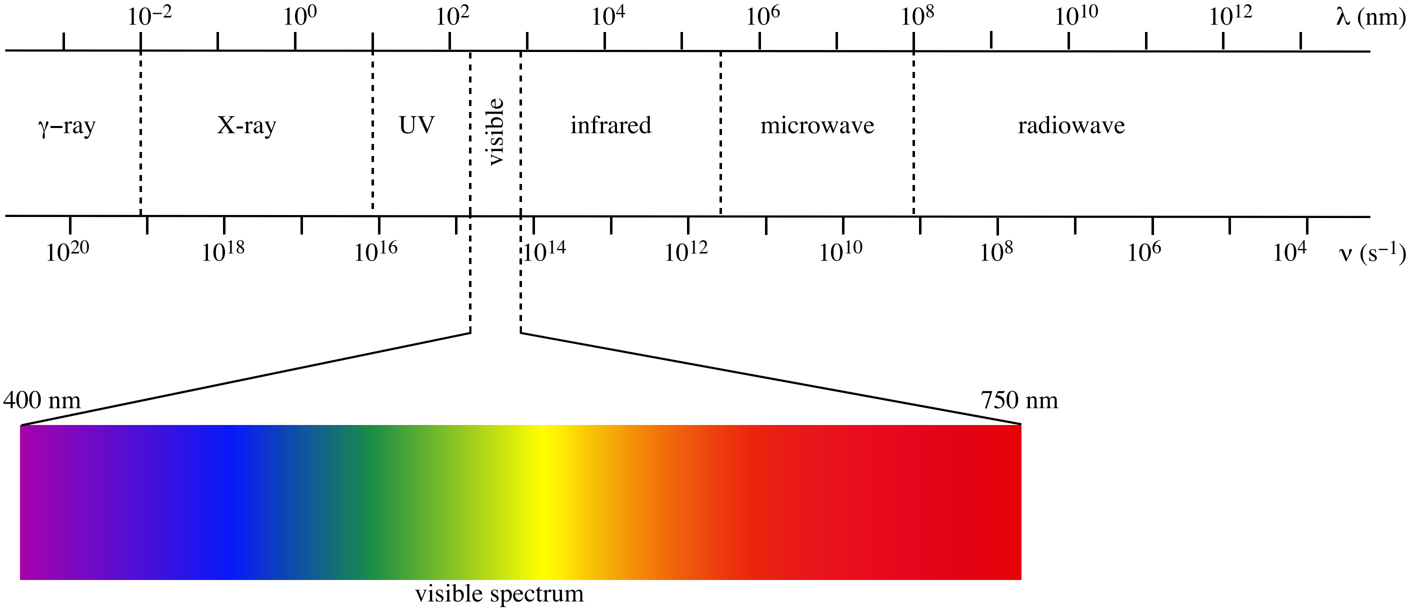
Lecture Notes
Chem 51A
S. King

Chapter 13
Infrared Spectroscopy

I. Background

Nearly every portion of the electromagnetic spectrum has been used to elucidate the structures of atoms and molecules.

The Electromagnetic Spectrum:



A variety of techniques are available, including ***Ultraviolet/Visible*** (UV/Vis) ***Infrared*** (IR) and ***Nuclear Magnetic Resonance*** (NMR) Spectroscopy.

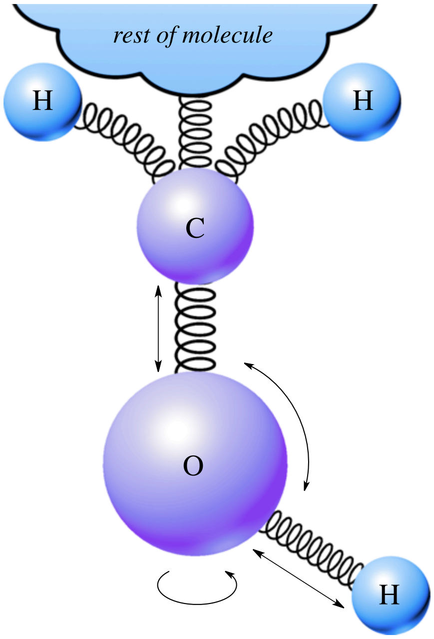
These techniques are based on the fact that molecules have different kinds of energy levels, and therefore absorb radiation in several regions of the electromagnetic spectrum. When a molecule absorbs light of a given frequency, specific molecular effects occur, depending on the wavelength absorbed. Low energy radiowaves, for example, cause nuclear spin flip transitions, whereas more energetic UV radiation results in electrons being promoted to higher energy levels. Energy is proportional to the frequency of light absorbed:

Molecular effects associated with different regions of the EM spectrum:

Wavelength (λ)		**Energy/mole**	**Molecular effects**
10^{-10} meter	gamma rays	10^{6} kcal	
10^{-8} meter	X-rays	10^{4} kcal	ionization
	vaccum UV	10^{2} kcal	
	near UV		electronic transitions
10^{-6} meter	visible	10 kcal	
10^{-4} meter	infrared (IR)	1 kcal	molecular vibrations
10^{-2} meter	microwave	10^{-2} kcal 10^{-4} kcal	rotational motion
10^{0} meter 10^{2} meter	radio	10^{-6} kcal	nuclear spin transitions

II. IR Spectroscopy

IR radiation causes groups of atoms to vibrate with respect to the bonds that connect them.



✷ *We will mostly be concerned with stretching vibrations because bending vibrations occur in a region of the spectrum that is difficult to interpret.*

A. The frequency of the stretching vibration depends on two quantities:

$\mathbf{m_1}$ and $\mathbf{m_2}$: the masses of the atoms
f: the force constant, or spring constant (a measure of the stiffness of the bond)

- Heavier atoms vibrate more slowly than lighter ones.
- The force constant is larger for stronger bonds (it takes more energy to stretch a stronger bond) and smaller for weaker bonds, thus stronger bonds usually vibrate at a higher frequency than weaker bonds between similar atoms.

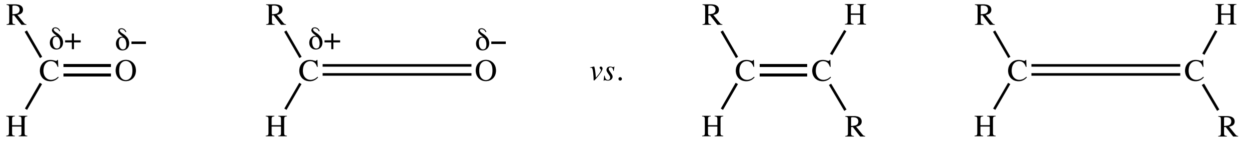
Examples:

1. O—H
C—H

2. ≡
=
—

3. H—C_{sp}
H—C_{sp2}
H—C_{sp3}

B. The intensity of the absorption is proportional to the strength of the dipole moment of the molecule.



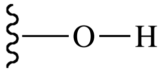
polar bond

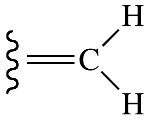
non-polar bond

∴ A symmetrical bond with no dipole moment will show only a weak absorption or none at all.

$H_3C-\equiv-CH_3$

C. For a given type of bond, the frequency shows little change with the rest of the molecule.





∴ **IR is especially useful in indicating the functional groups present in a molecule.**

How do you interpret an IR spectrum?

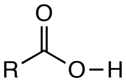
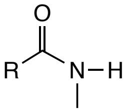
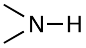
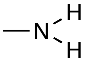
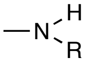
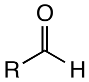
1) You will usually be given the molecular formula of the compound. Use it to evaluate the units of unsaturation *(see Chapter 10.)*
2) Divide the spectra into 3 regions, and look for characteristic bands using the IR chart given:

    X-H region
    sp region
    double bond region

3) Practice, practice, practice!

Interpretation of Infrared Spectra

X-H Region

Phenol & Alcohols	RO−H	3700 - 3500 sharp or 3200 - 3600 broad (H-bonded)	
Acids		2800 - 3600 very broad	
Amines & Amides	 	3300 - 3500	2 bands:  primary 1 band:  secondary
C-H Bonds	C≡C−H	3200 -3300	
	C=C−H	3000 - 3200	
	C−C−H	2900 - 3000	
		2700 -2800	

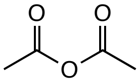
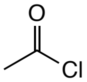
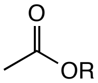
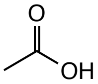
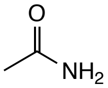
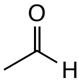
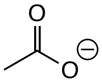
sp Region

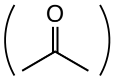
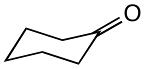
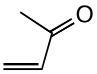
Acetylenes	C≡C	2100 (weak or absent if highly symmetrical)
Nitriles	C≡N	2200
Carbon dioxide	O=C=O	2350

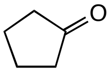
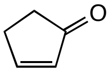
Double Bond Region

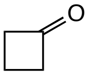
Alkenes	C=C	1600 - 1670 weak unless conjugated
Imines	C=N	1600 - 1700
Nitro	—NO_2	1350 and 1550

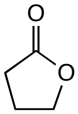
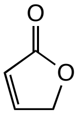
Carbonyl Groups:

Anhydrides		1800 - 1840 (2 bands)
Acid Chlorides		1800
Esters		1725 - 1750
Acids		1710
Amides		1650
Aldehydes		1725
Carboxylate		1550-1610 and 1400

Ketones: Acyclic  and  1710  1680

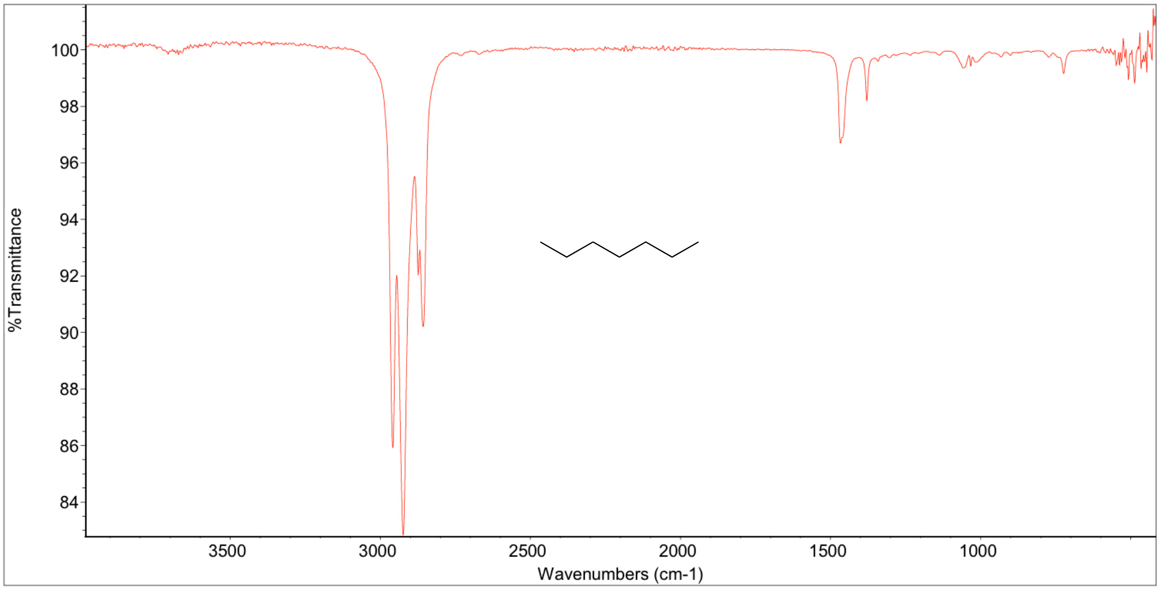
 1740  1715

 1770

 1770  1740

Ring Contraction:
add 30 for each contraction

Conjugation:
subtract 30


%Transmittance
100
98
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86
84
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1500
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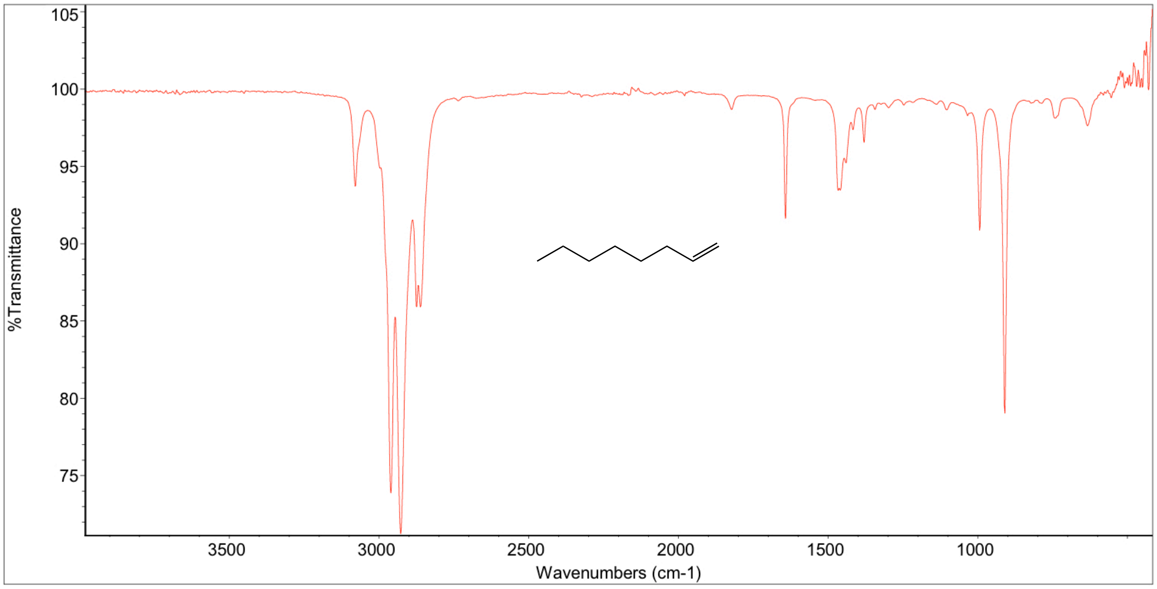
Wavenumbers (cm-1)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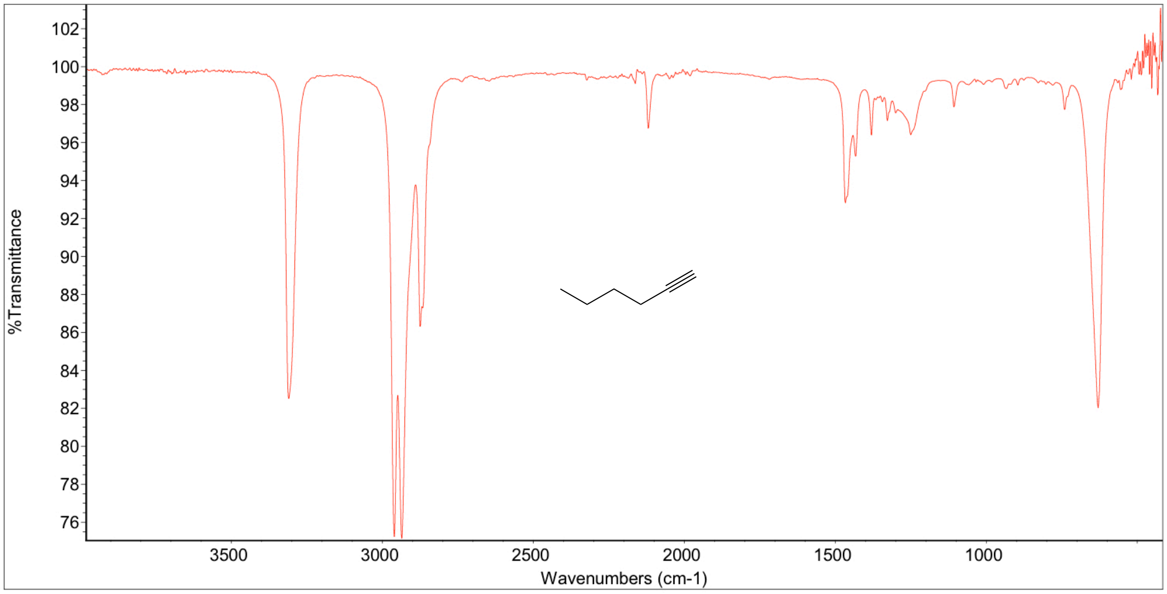
Wavenumbers (cm-1)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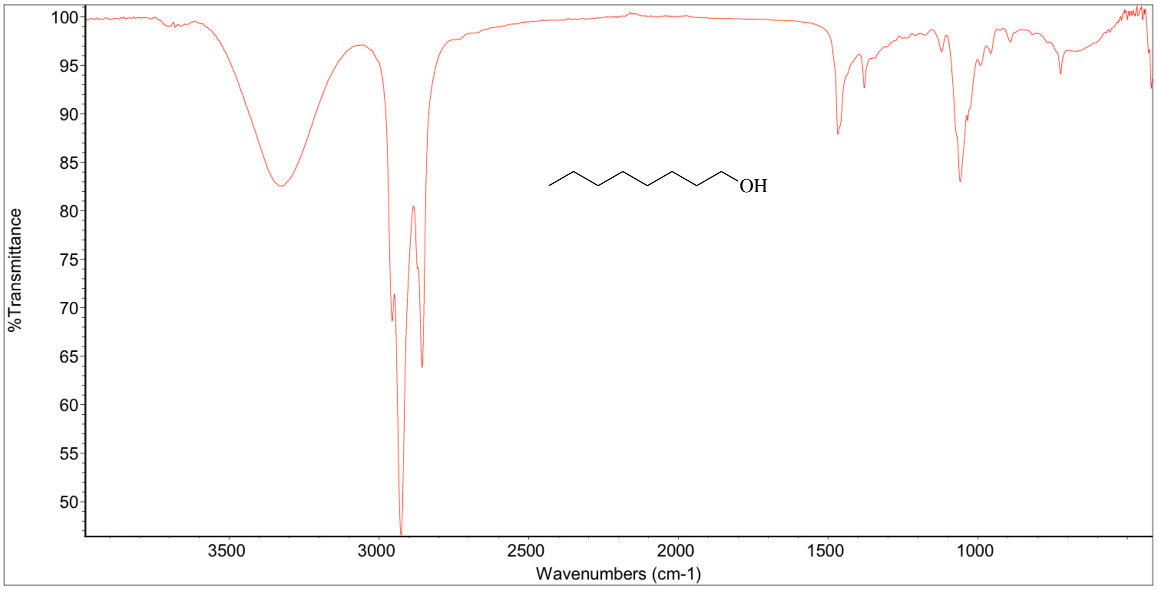
Wavenumbers (cm-1)


%Transmittance
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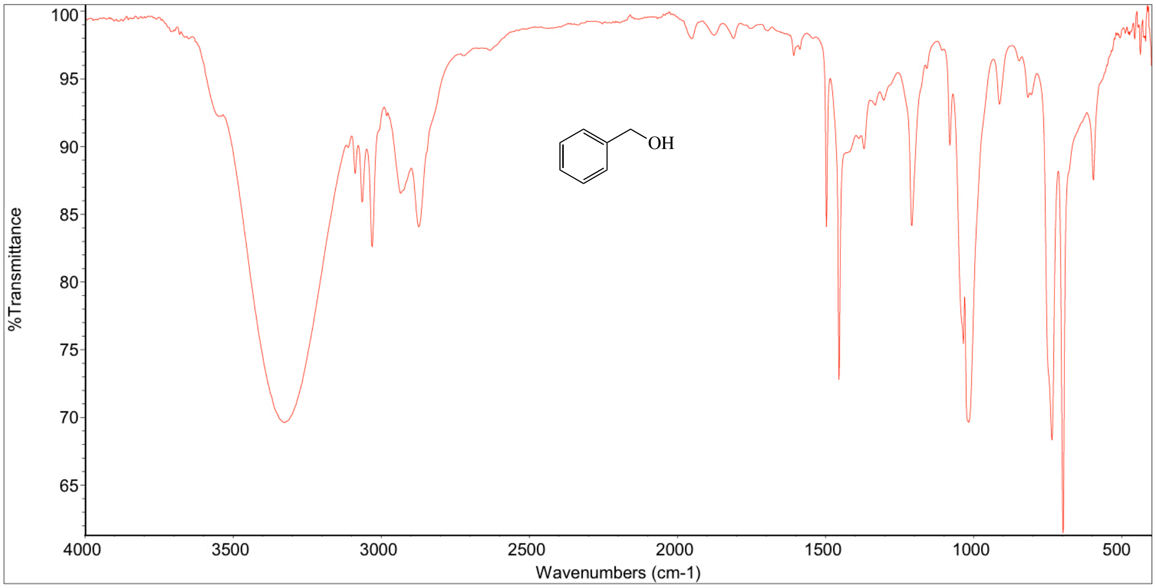
Wavenumbers (cm-1)
OH


%Transmittance
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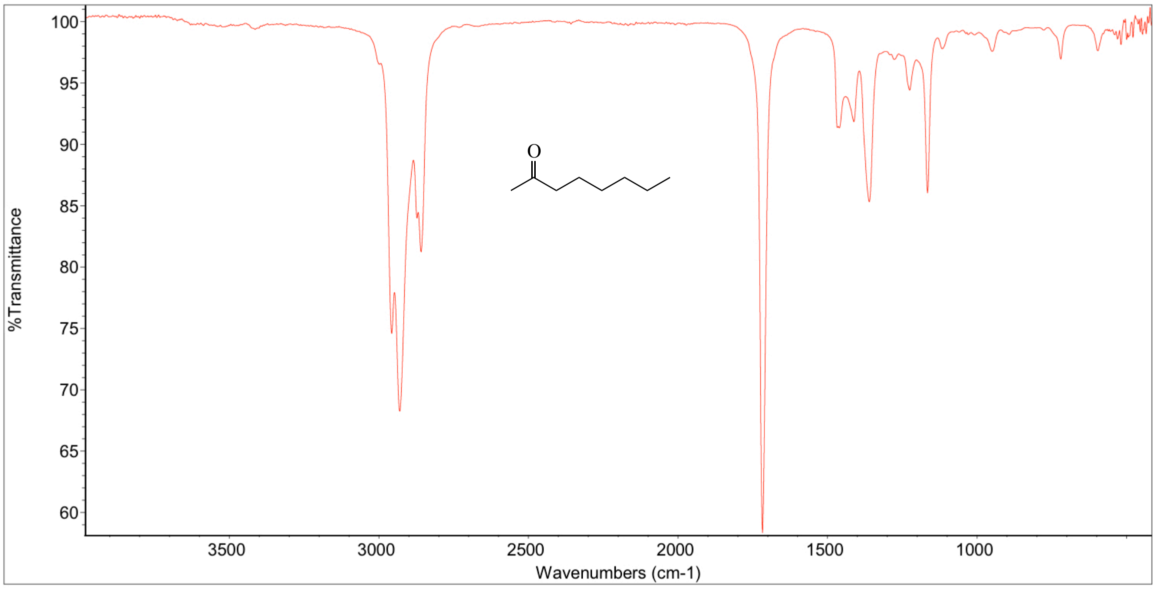
1000
500
Wavenumbers (cm-1)
OH


%Transmittance
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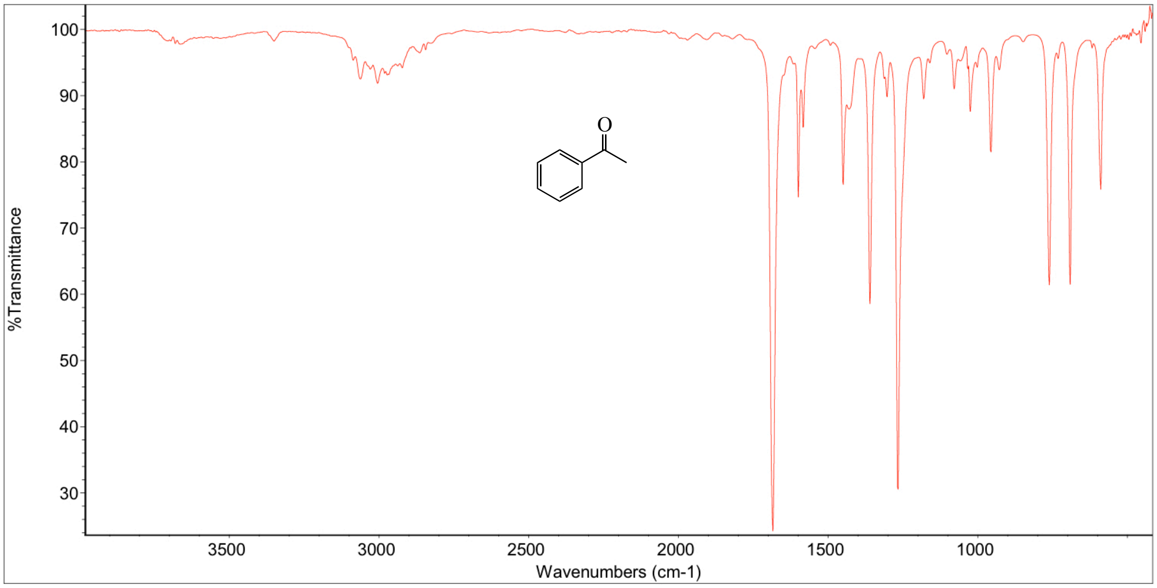
Wavenumbers (cm-1)
O


O
%Transmittance
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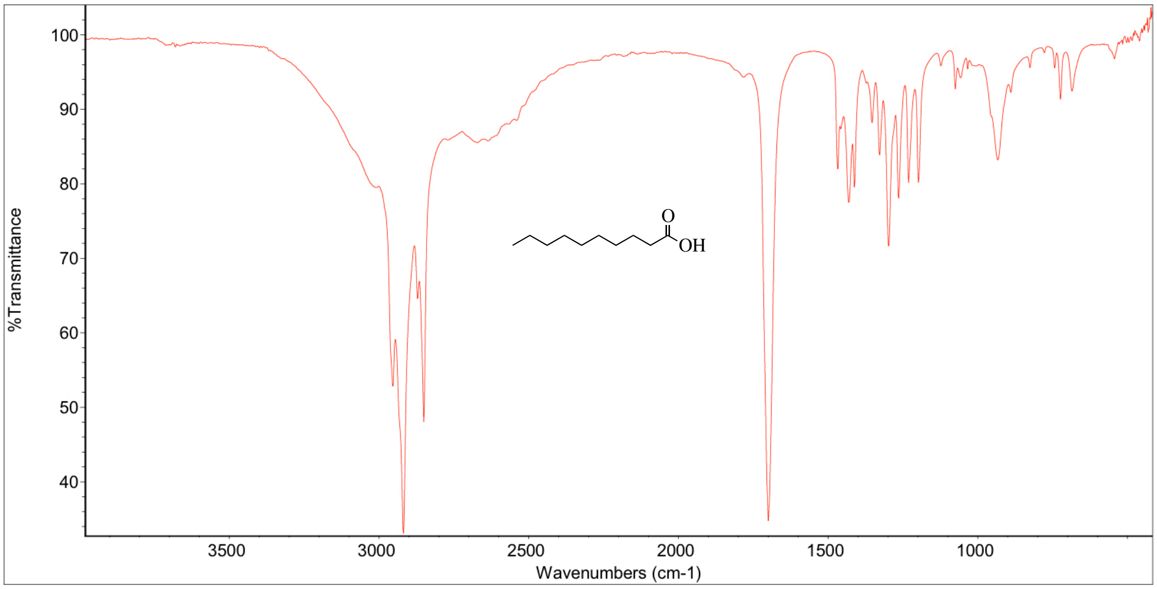
Wavenumbers (cm-1)


O
OH
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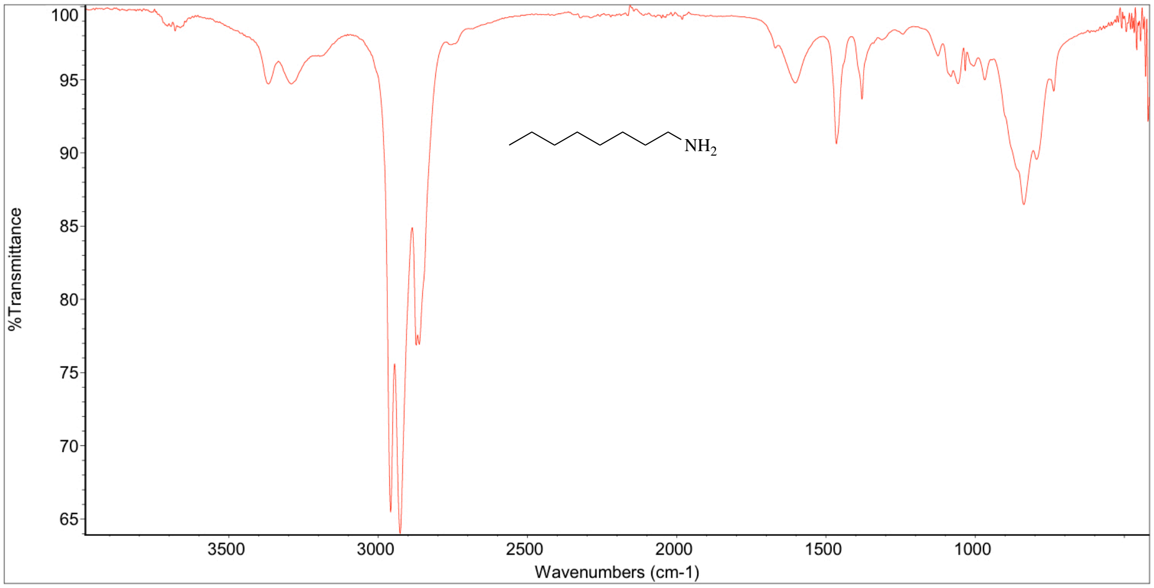
Wavenumbers (cm-1)


NH$_2$
%Transmittance
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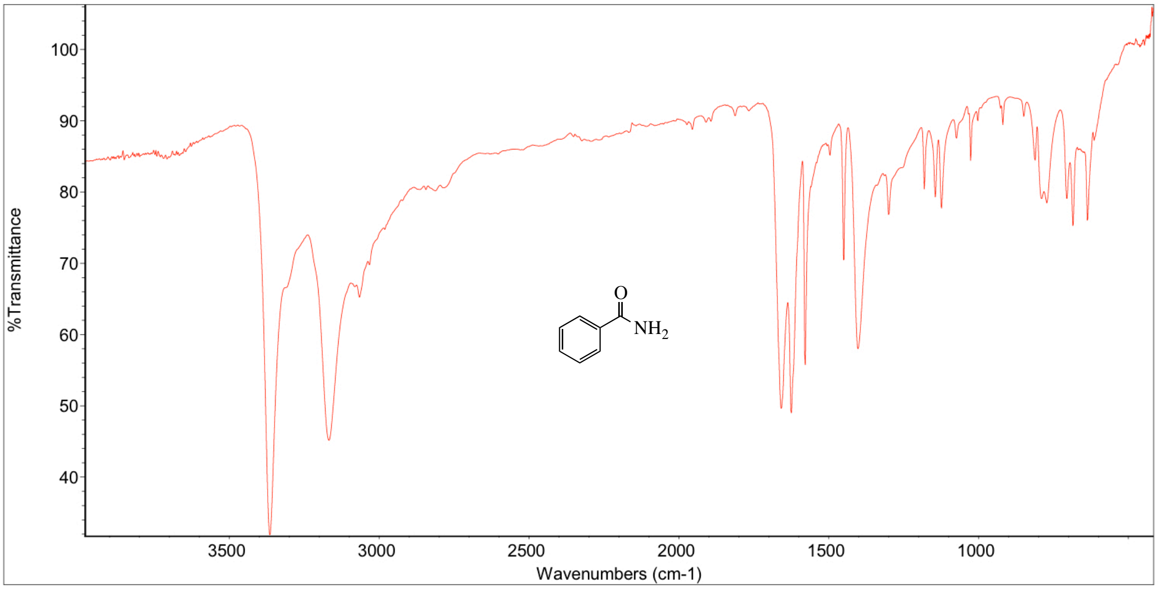
1000
Wavenumbers (cm-1)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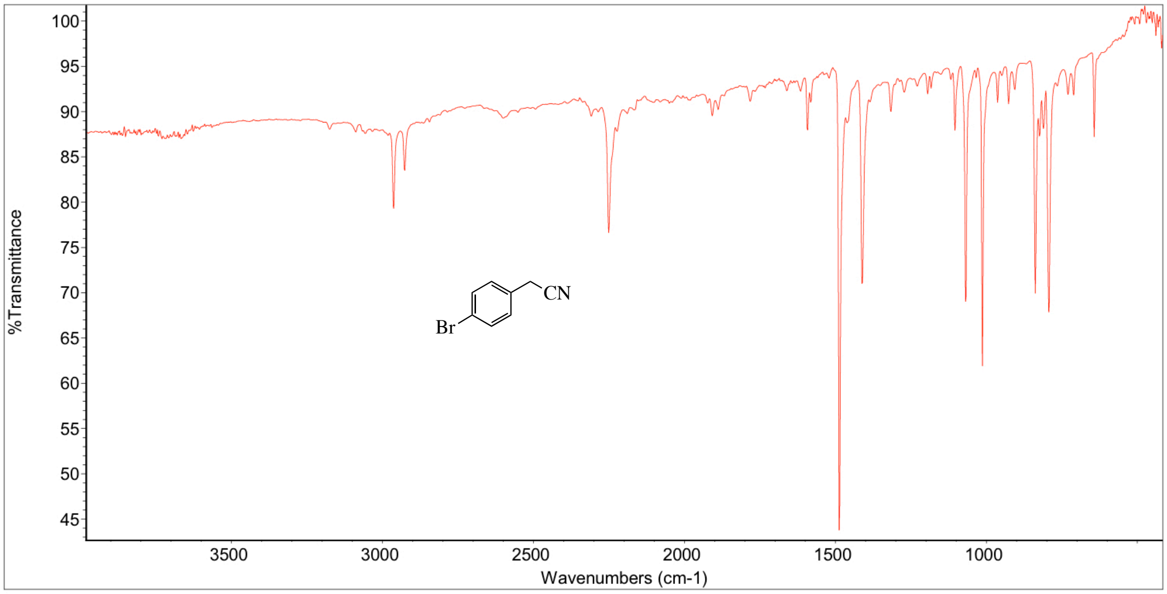
Wavenumbers (cm-1)
O
NH$_2$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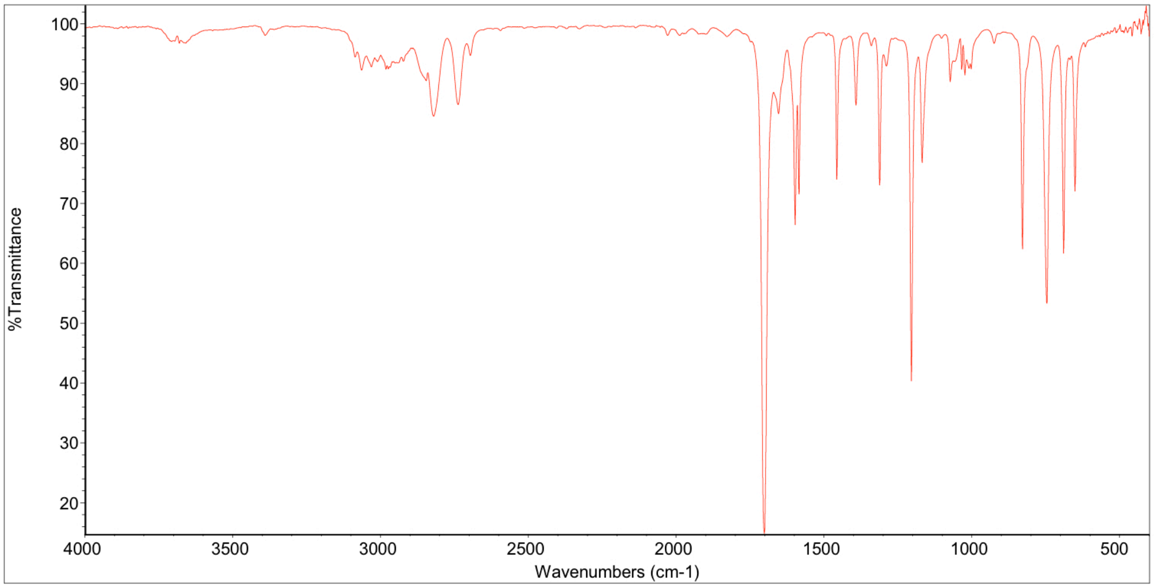
Wavenumbers (cm-1)
Br
CN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Wavenumbers (cm-1)