Infra-Red Spectroscopy
3 – Spectra Analysis

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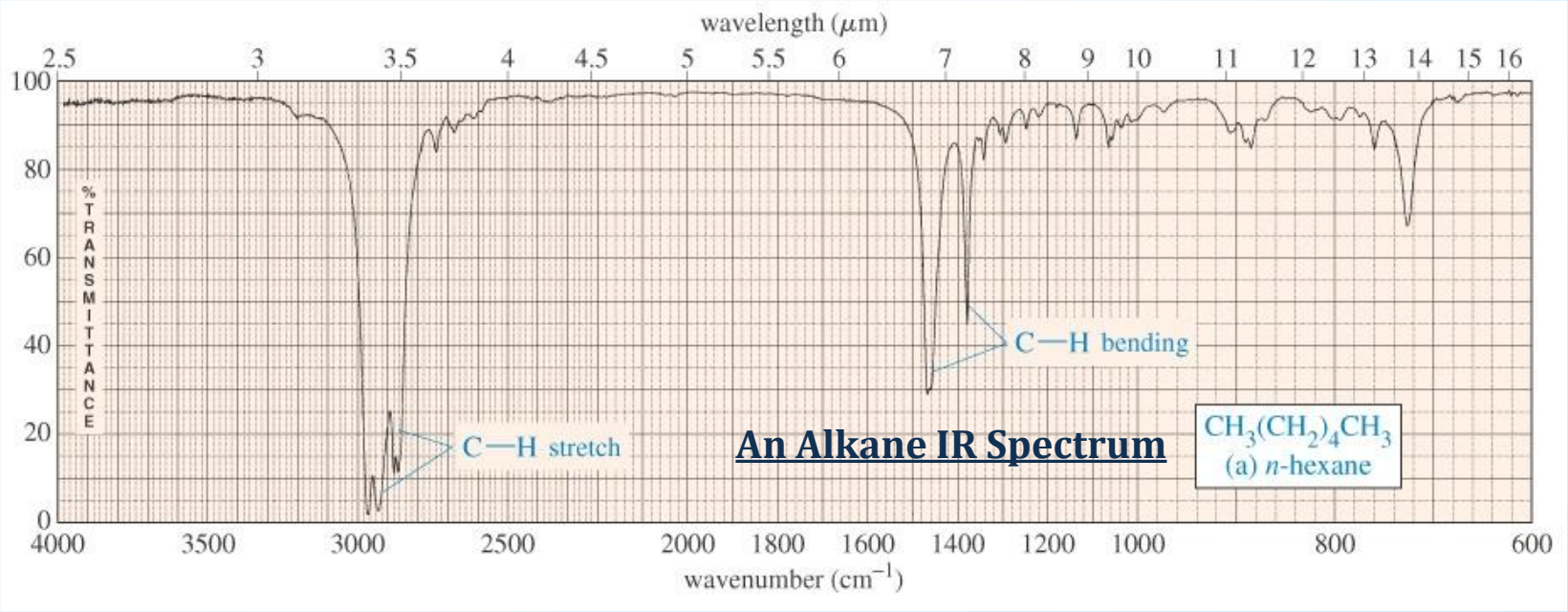
Hydrocarbons

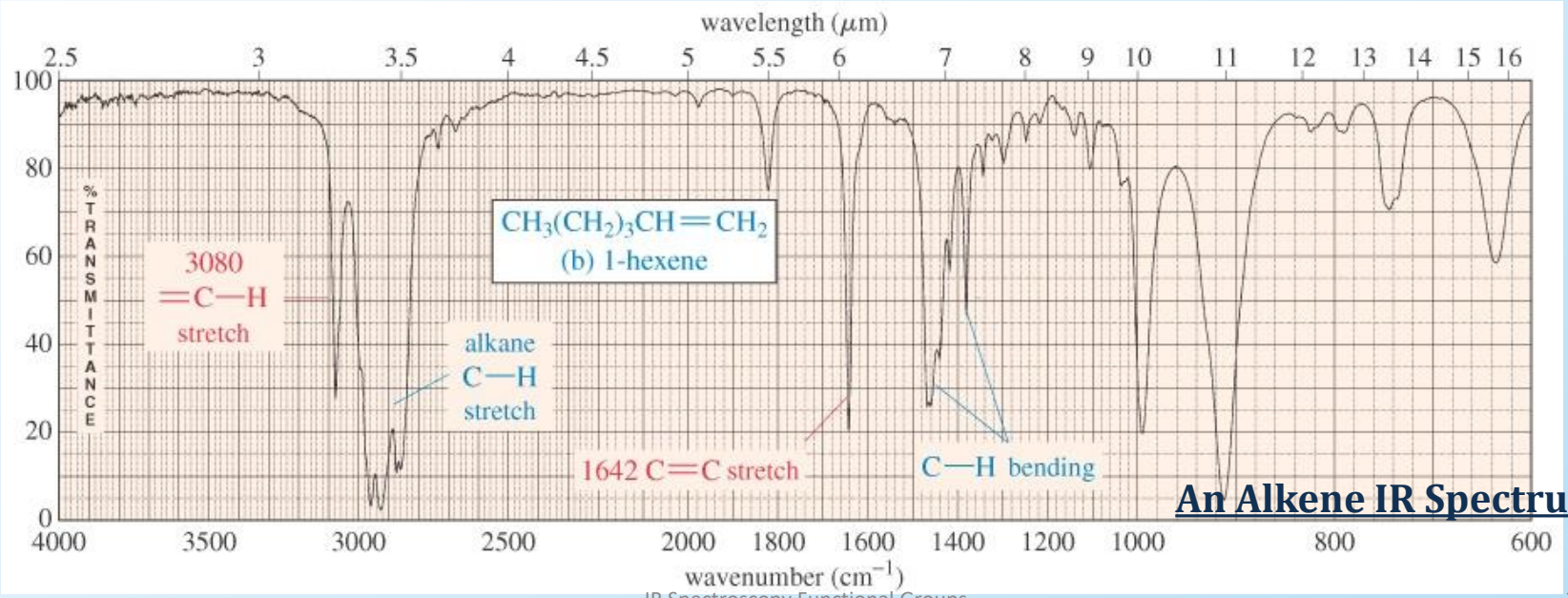
Hydrocarbons have the C-C stretches as well has C-H stretches.

C-H stretches occur around 3300 cm^{-1}. The C-C bonds appear in the fingerprint region. We will look at three hydrocarbons.

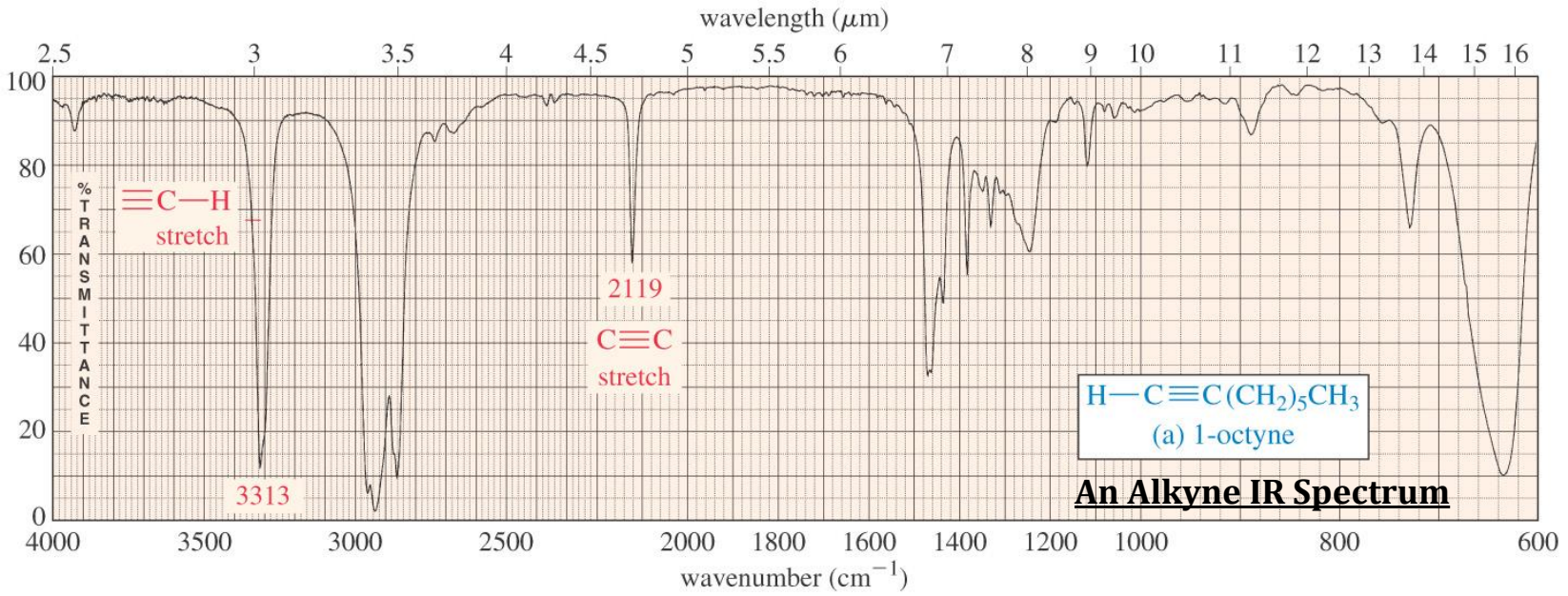
Alkanes	C-H	3000 cm^{-1}	This is the most common backbone of all organic compounds. The C-H signals will always appear in all compounds that have sp^3 hybridized carbons
Alkenes	=C-H C=C	3100-3000 cm^{-1} ~1660 cm^{-1}	Alkenes will have two characteristic signals: one is =C-H stretch and the other is C=C. The =C-H signal depends on the location of double bond and depends on the number of alkyl groups around it. The C=C signal is absent in case the alkene is symmetrical.
Alkynes	≡C-H C ≡ C	~3300 cm^{-1} ~2100 cm^{-1}	Alkynes will have two characteristic signals: one is ≡C-H stretch and the other is C ≡ C. The ≡C-H signal will appear only in terminal bonds. The C ≡ C signal is absent in case the alkyne is symmetrical.

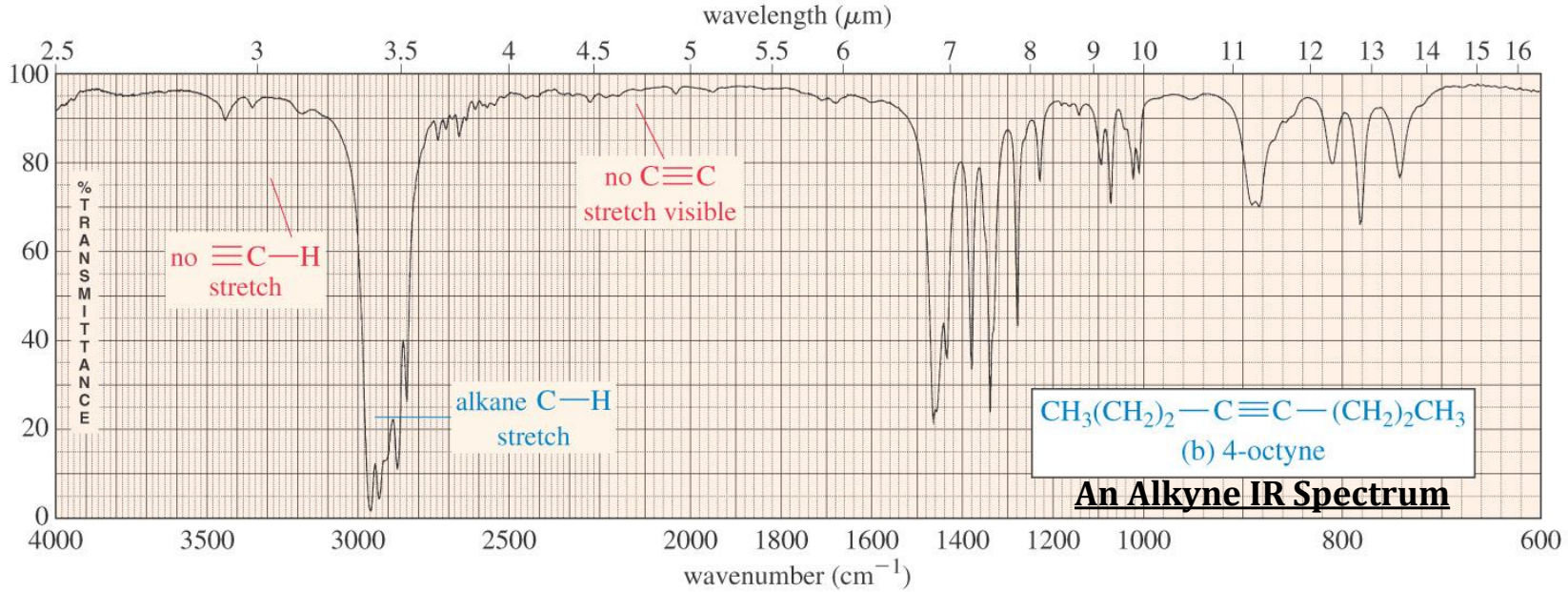


An Alkane IR Spectrum



An Alkene IR Spectrum

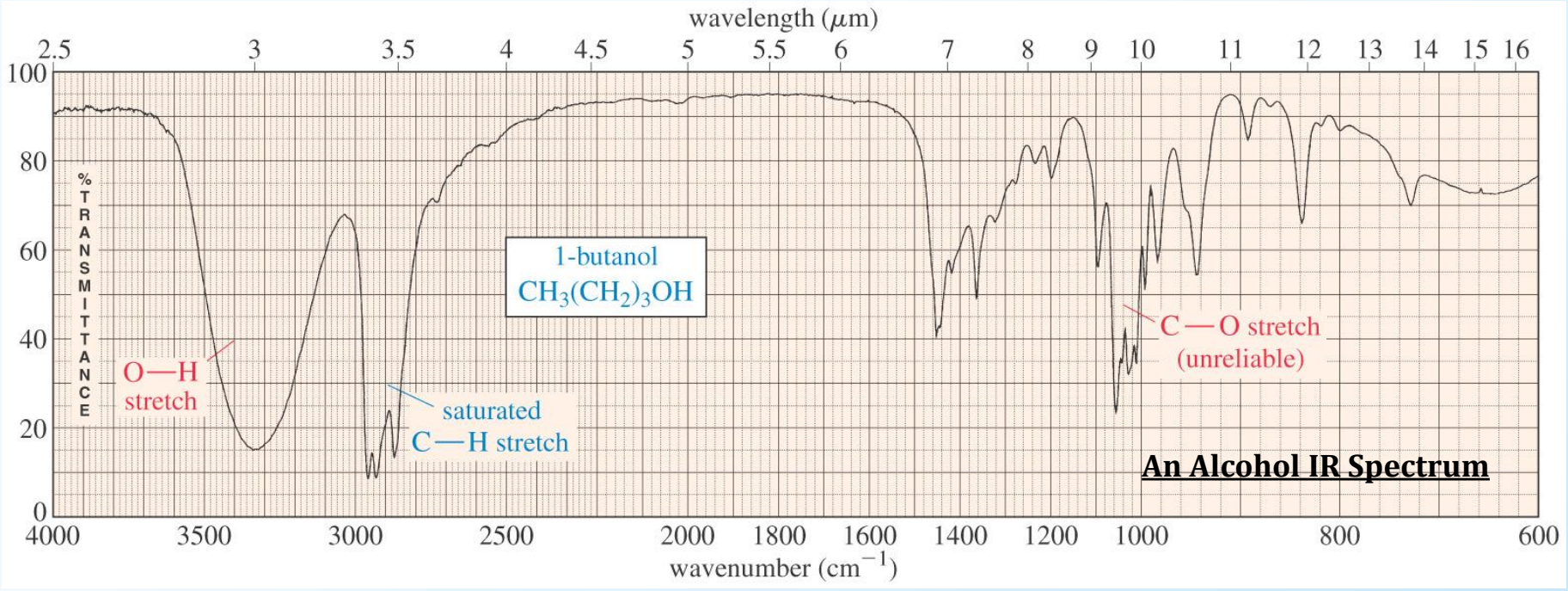




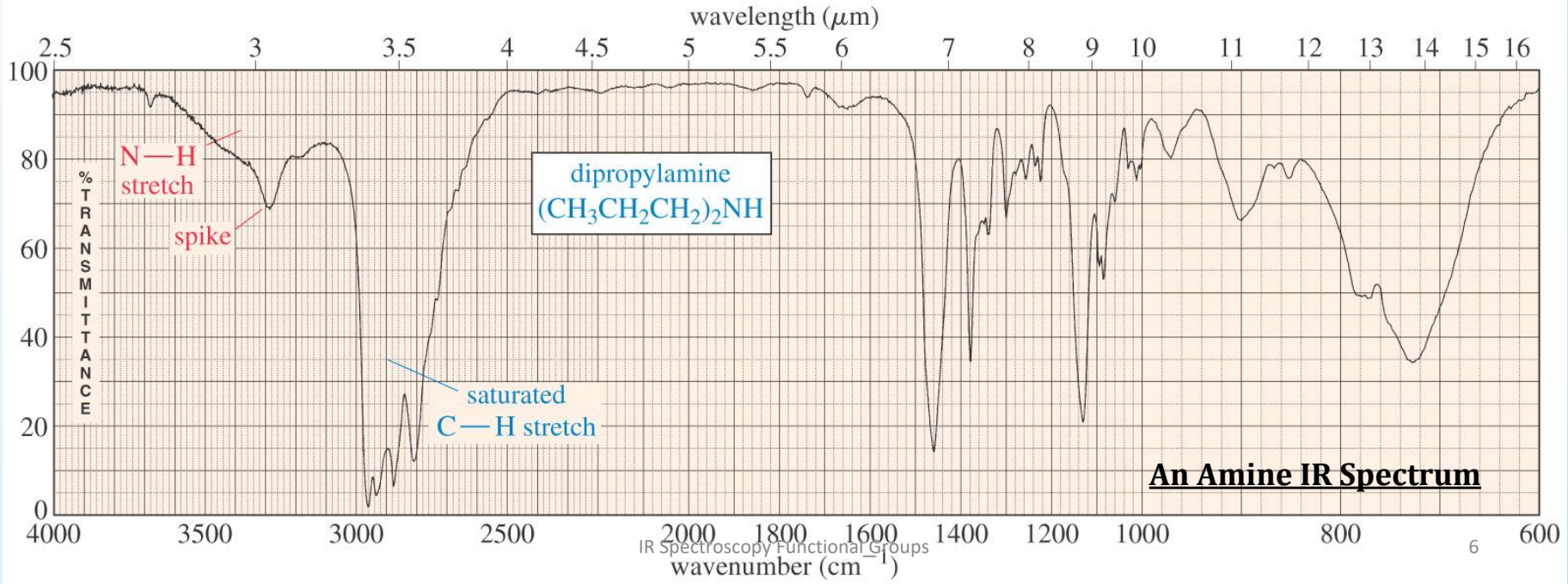
O-H and N-H Stretching

Both O-H and N-H signals appear around 3300 cm^{-1}, but they look different.

Alcohols	O-H	~3500 cm^{-1}	The O-H signal shows up prominently in the IR. It is an intense broad signal due to H-bonding.
Amines	N-H	3300-3500 cm^{-1}	Amines are similar to OH in the region they appear. They are not as broad in appearance. The number of signals seen depend on how many Hs are on the N. 2H (1^o amine) show 2 peaks, 1H (2^o amine) has one peak and no H (3^o amine) has no peaks.

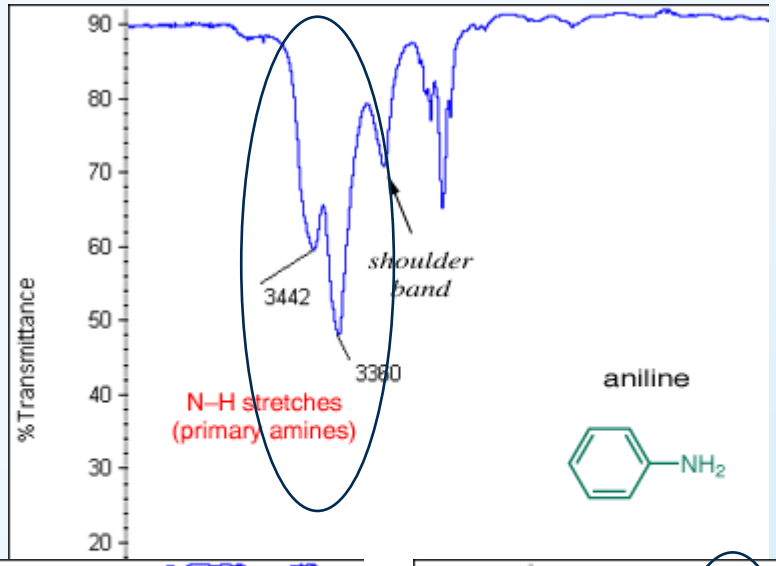


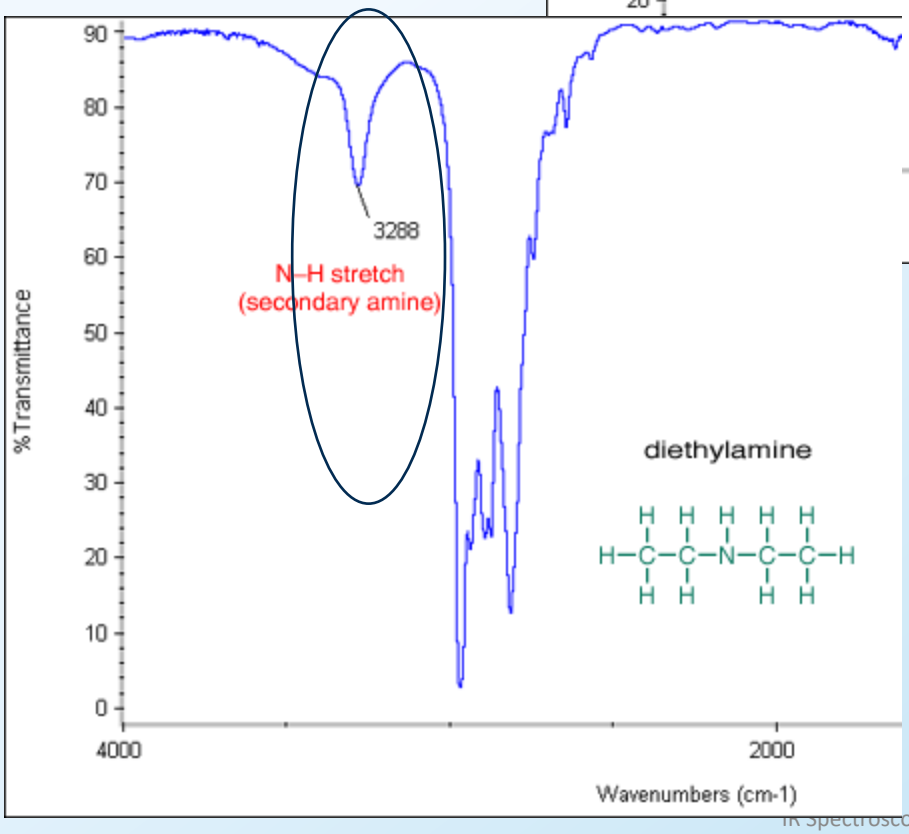
An Alcohol IR Spectrum

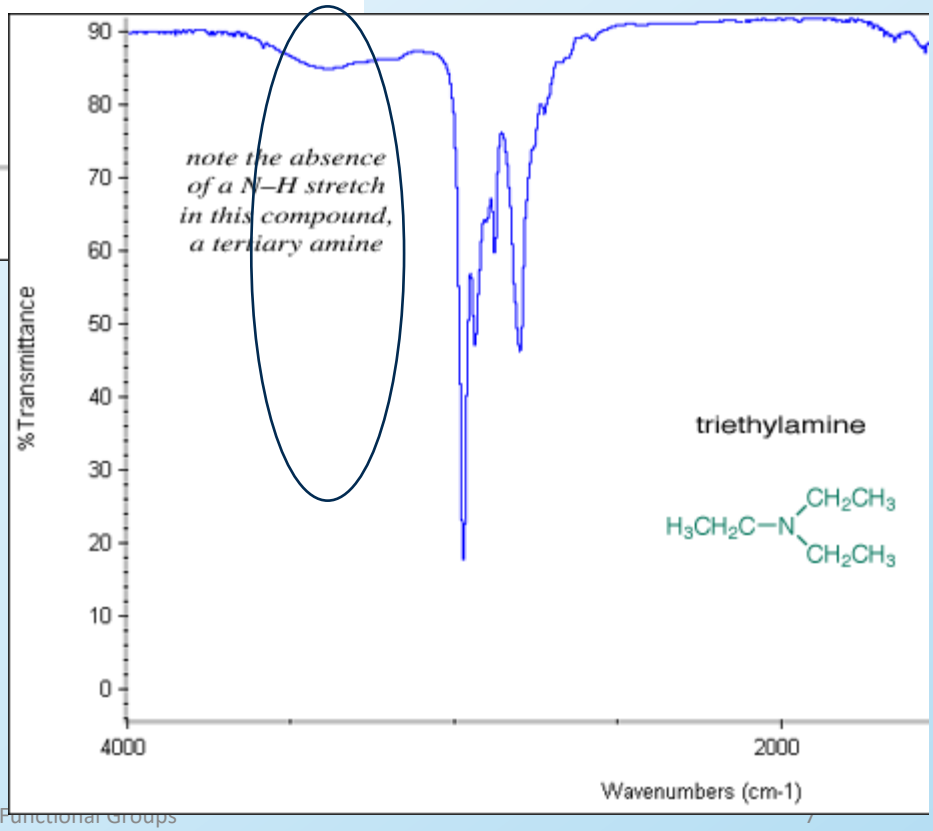


An Amine IR Spectrum

Amines







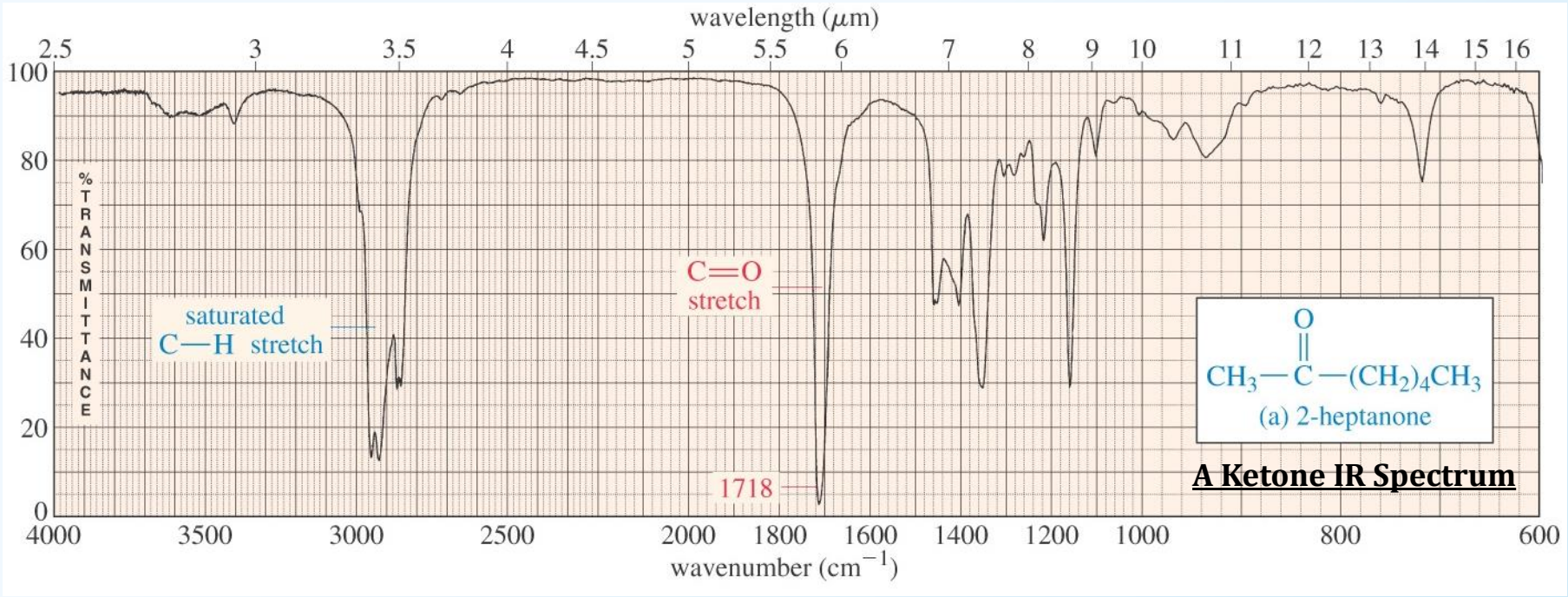
https://www.orgchemboulder.com/Spectroscopy/irtutor/aminesir.shtml

Carbonyl Stretching

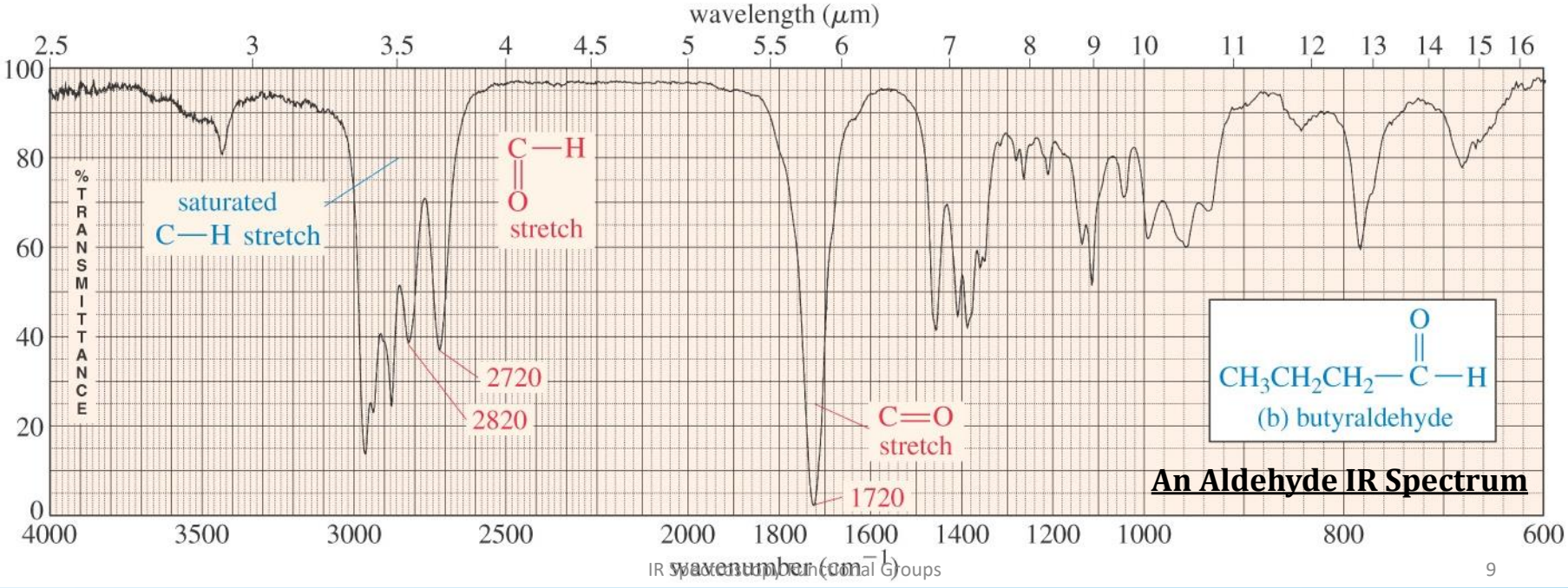
There are a variety of carbonyl, C=O, bonds in organic chemistry: aldehyde, ketone, carboxylic acid, carboxylic ester and amides. On careful examination of the location of peaks one can determine which functional group the C=O bond belongs to.

Carbonyls give a strong IR signal around 1710-1720 cm^{-1}, so it is easy to recognize.

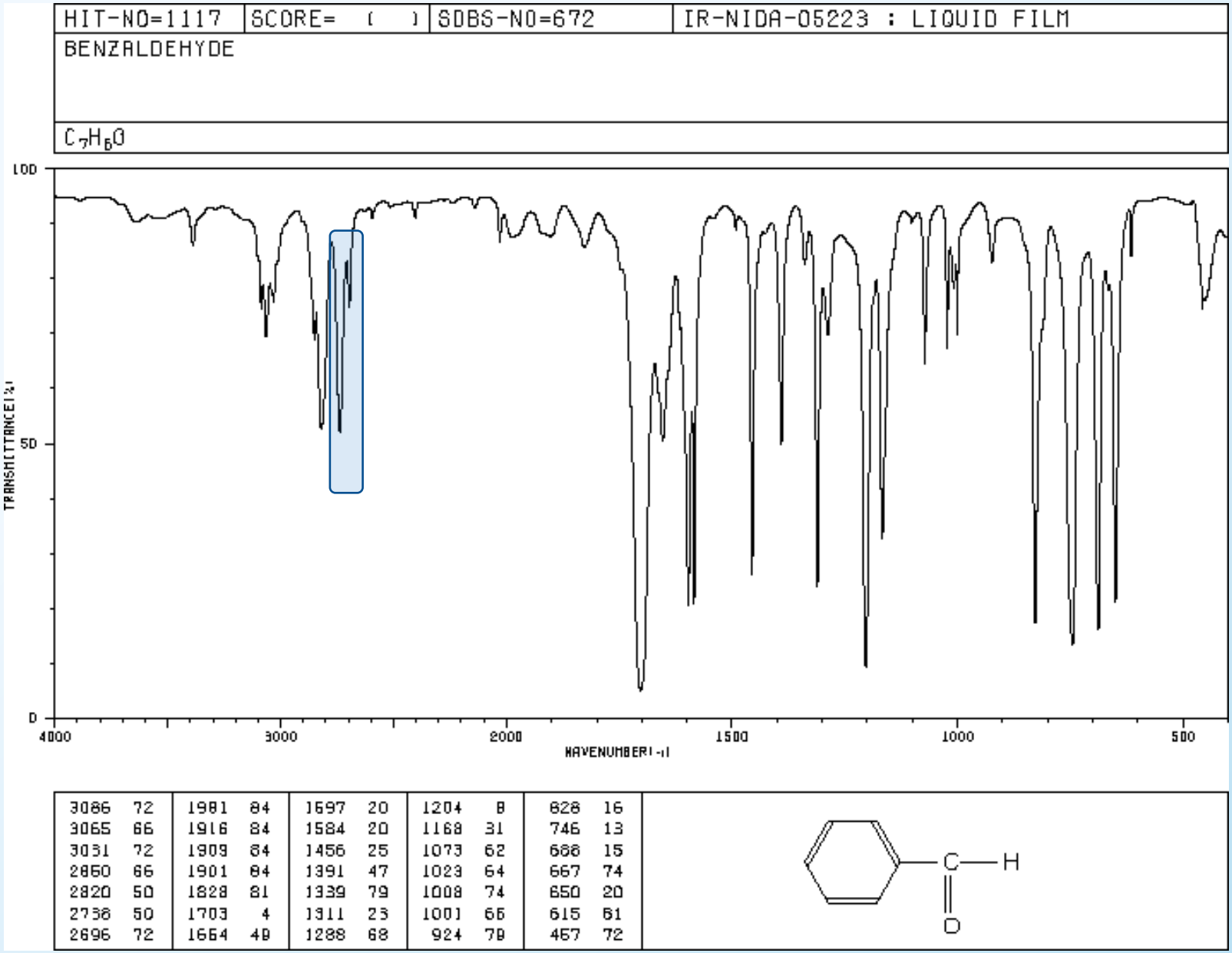
Ketones	C=O	~1730 cm^{-1}	Only the C=O bond will show for ketones
Aldehydes	C=O O=C-H	~1730 cm^{-1} 2700 and 2800 cm^{-1}	In addition to C=O they will have two additional C-H signals from the O=C-H
Carboxylic Acid	C=O -OH	~1700 cm^{-1} 3300 cm^{-1}	In addition to C=O they will also have O-H signal.
Carboxylic Esters	C=O	1730-1740 cm^{-1}	These are the hardest to identify as their signal might look like ketone. The C=O of an ester absorbs at little bit higher frequency. Usually, additional spectroscopy or qualitative information is helpful in deciding for esters.
Amides	C=O N-H	~1640 cm^{-1} 3300 cm^{-1}	These will show a C=O signal towards the higher energy region. And depending on the number of alkyl groups on N, there might be signals in the N-H region..



A Ketone IR Spectrum



An Aldehyde IR Spectrum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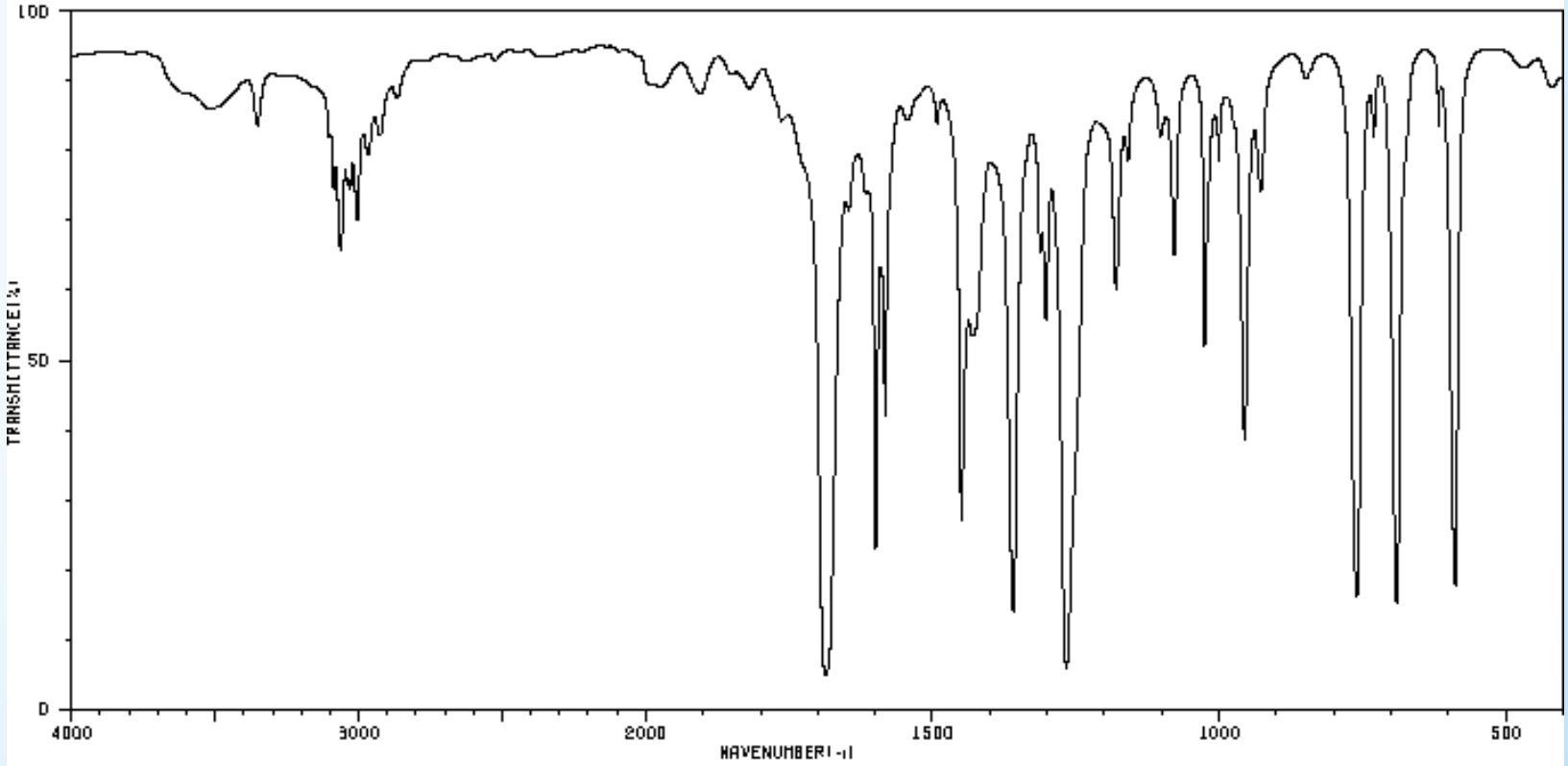
SCORE= ( )
SDBS-NO=672
IR-NIDA-05223 : LIQUID FILM
BENZALDEHYDE
C7H6O
100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
3086 72
3065 66
3031 72
2860 66
2820 50
2738 50
2696 72
1981 84
1916 84
1909 84
1901 84
1828 81
1703 4
1664 49
1697 20
1584 20
1456 25
1391 47
1339 79
1311 23
1288 68
1204 8
1168 31
1073 62
1023 64
1008 74
1001 66
924 79
828 16
746 13
686 15
667 74
650 20
615 61
457 72
C
H
O

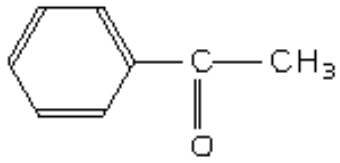
HIT-NO=1153	SCORE= ( )	SDBS-NO=722	IR-NIDA-05227 : LIQUID FILM

ACETOPHENONE

C_8H_8O

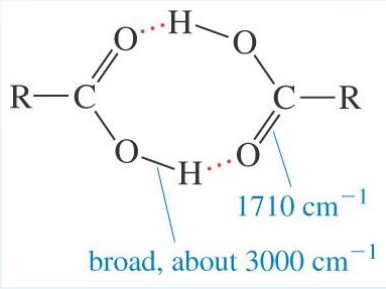


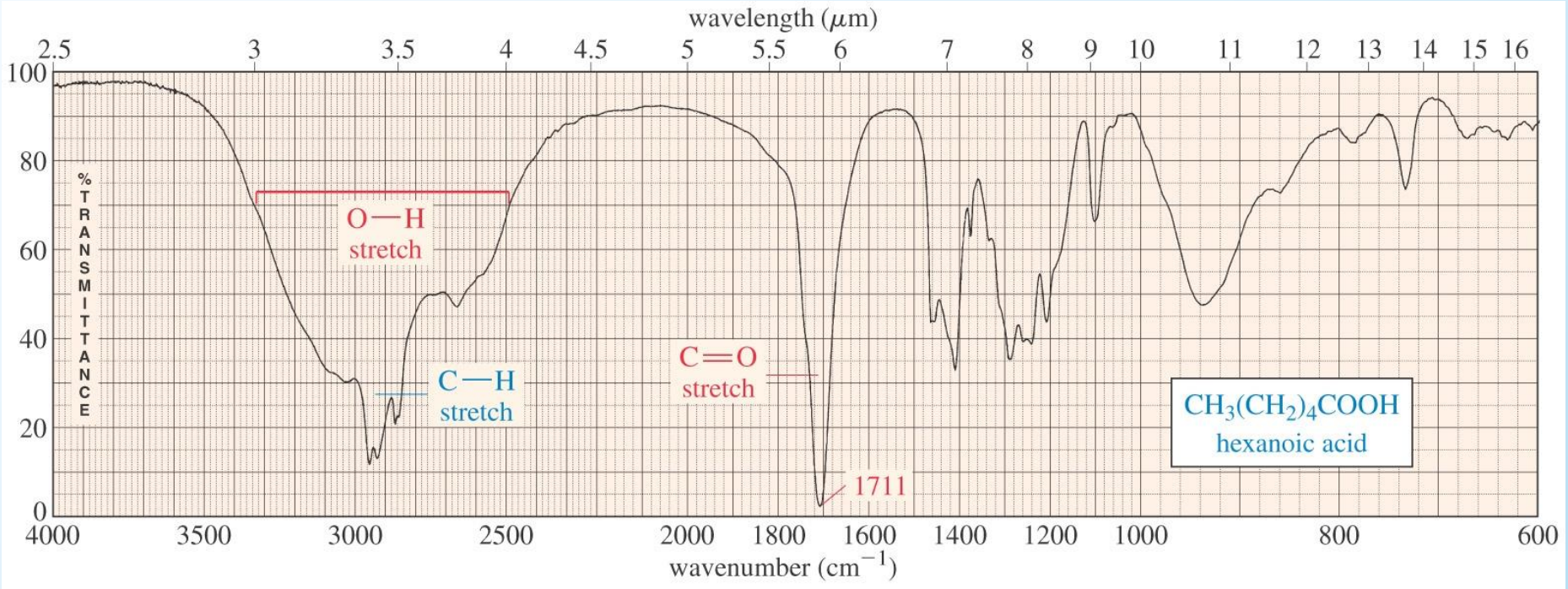
3604	84	2967	77	1646	81	1267	6	966	37
3352	81	2925	79	1492	81	1181	58	928	72
3087	72	2867	84	1450	26	1160	74	761	15
3063	64	1686	4	1430	62	1103	79	731	79
3040	72	1646	68	1360	13	1079	62	691	14
3029	72	1599	21	1313	82	1025	50	618	61
3006	68	1583	41	1303	63	1001	74	688	17



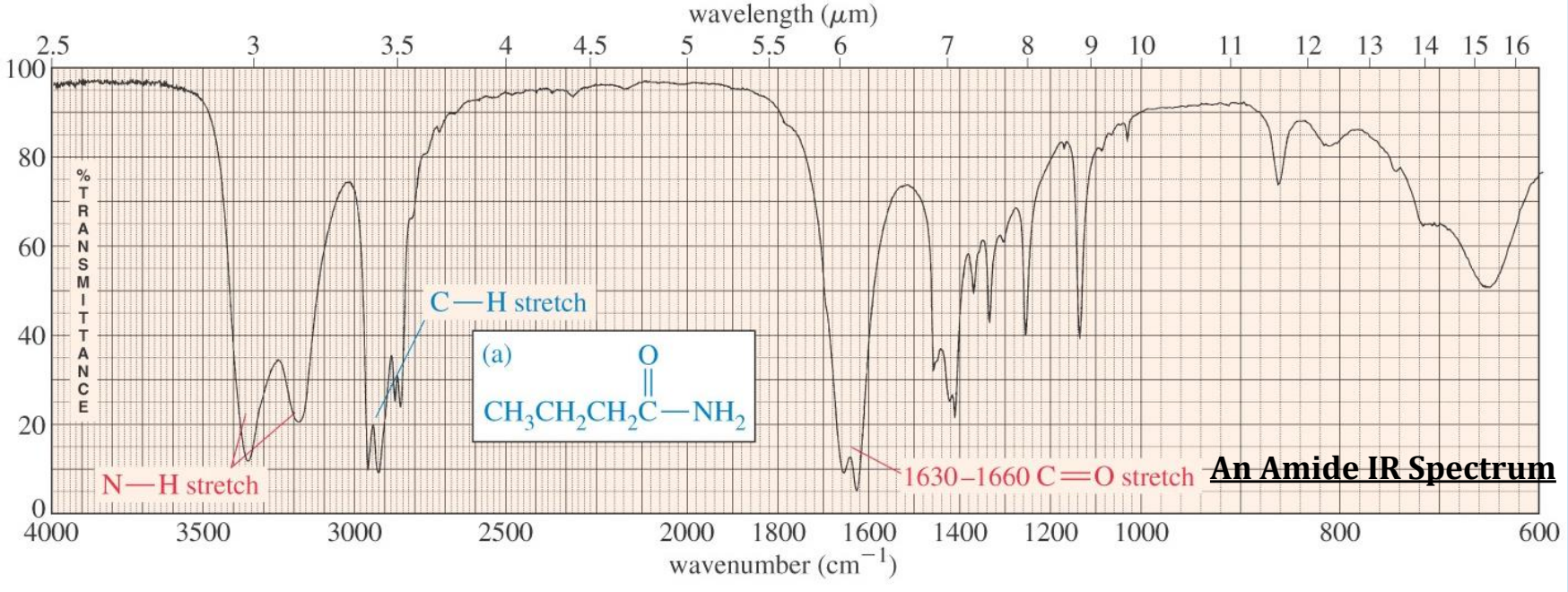
O-H Stretch of a Carboxylic Acid

This O-H absorbs broadly, 2500-3500 cm^{-1}, due to strong hydrogen bonding.





N-H Stretch of an Amide



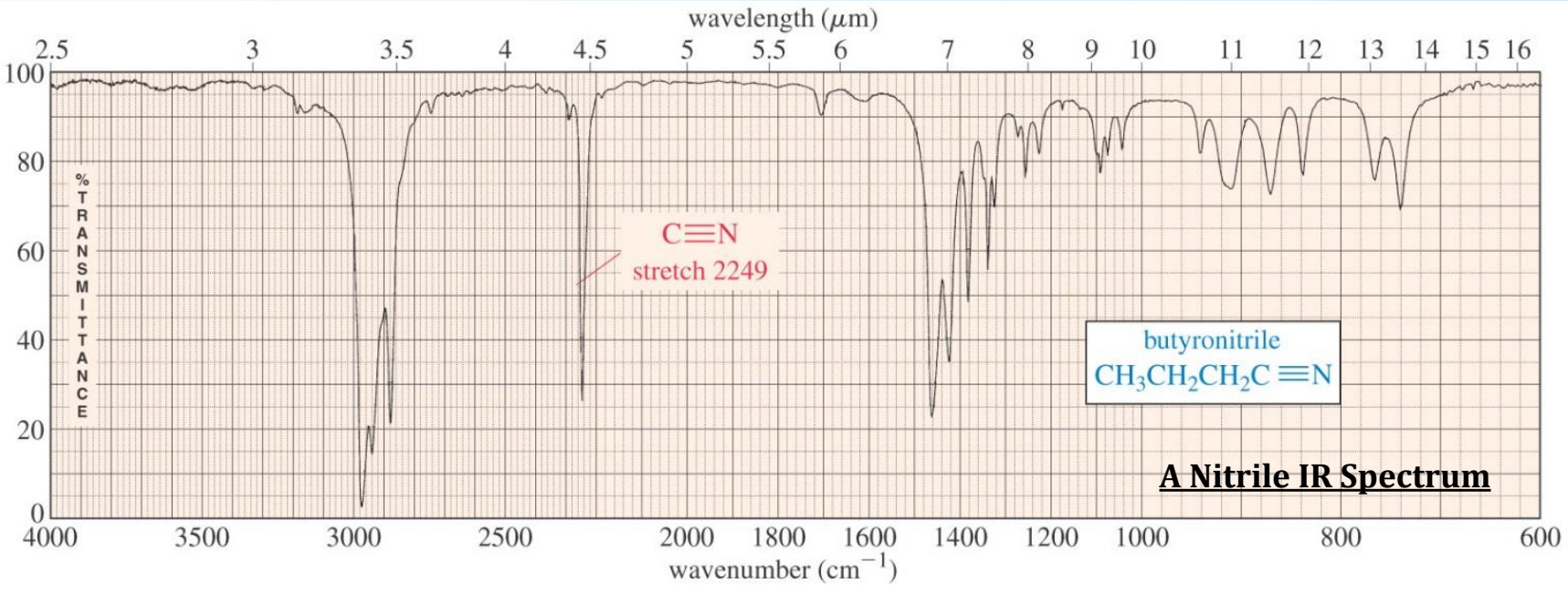
An Amide IR Spectrum

Carbon - Nitrogen Stretching

C - N absorbs around 1200 cm^{-1}, which is the fingerprint region.

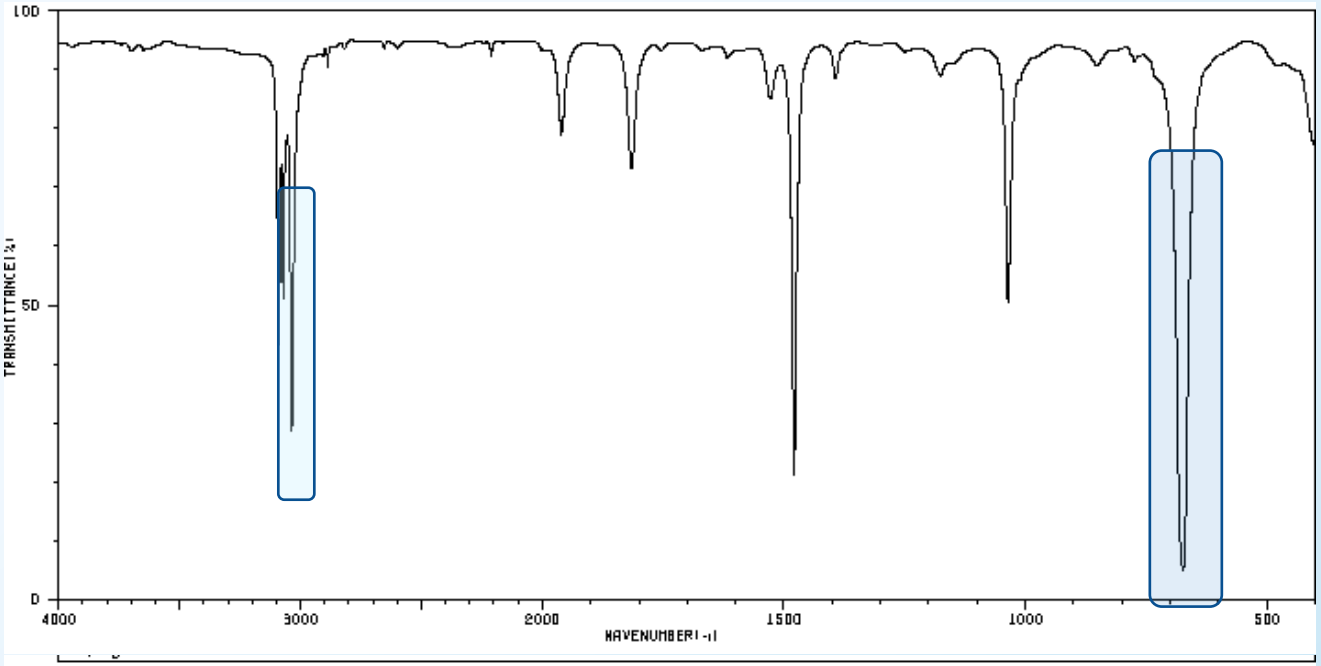
C = N absorbs around 1660 cm^{-1} and is much stronger than the C = C absorption in the same region.

C ≡ N absorbs strongly just *above* 2200 cm^{-1}. The alkyne C ≡ C signal is much weaker and is just *below* 2200 cm^{-1}.

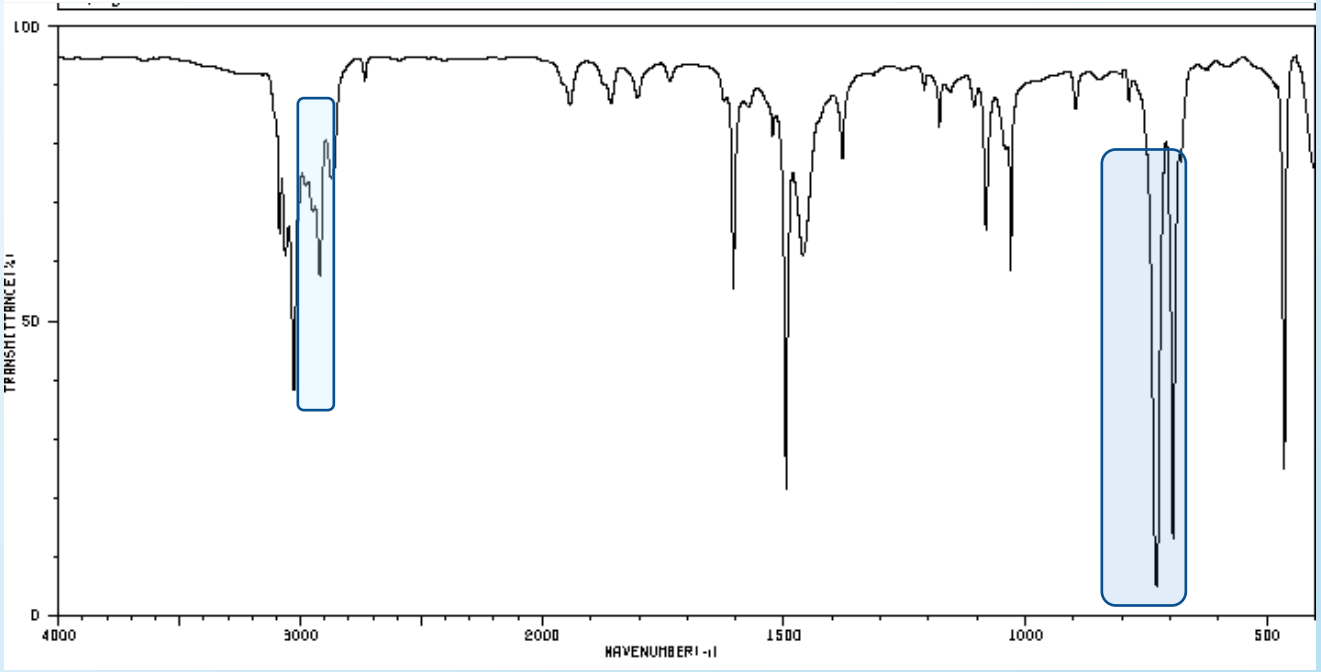


Aromatic

Benzene



Methylbenzene
(Mono substituted
Benzene)



Summary of IR Absorptions

3500 2500 1800 1600 400

Bonds to Hydrogen	Triple bonds	Double bonds	Single bonds
N - H O - H C - H	C ≡ C C ≡ N	C = C C = O C = N	C - C C - O C - N C - X

Fingerprint region

IR Chart

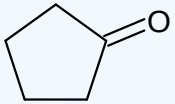
Organic Group	Specific Group	Range (cm^{-1})	Signal Intensity
Alkane			
	C-H	2852-2960	Strong
Alkene			
	=C-H	3010-3095	Medium
	C=C	1620-1680	Varies
	Cis RCH=CHR	675-730	Strong
	Trans RCH=CHR	960-975	Strong
Alkyne			
	≡C-H	3300	Strong
	C≡C	2100-2260	Sharp
Aromatic			
	Ar-H	~3030	
Substitution	Monosubstituted	690-710	Strong
	o-disubstituted	730-770	Strong
	m-disubstituted	735-775 and 770-810	Strong
	p-disubstituted	780-860	Strong
Alcohols			
	O-H	3590-3650	Strong
	Carboxylic acids O-H	2500-3000	Strong and broad
Carbonyls			
General	C=O	1630-1780	Strong
***Aldehydes**	CHO	1690-1740	Strong
Ketones	C=O	1680-1750	Strong
Carboxylic esters	COOR	1735-1750	Strong
***Carboxylic acids**	COOH	1710-1780	Strong
***Amides**	$CONH_2$	1630-1690	
Amines			
	N-H	3300-2500	Medium (1^o two peaks, 2^o, one peak and 3^o no peak)
Nitriles			
	C≡N	2220-2260	Medium and sharp

* More than one signal

Strengths and Limitations of IR

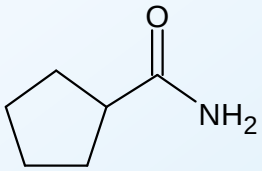
- IR alone cannot determine a structure.
- Some signals may be ambiguous.
- The *presence* of a functional group is generally a confirmation.
- The *absence* of a signal also may not be a definite proof that the functional group is absent, e.g., a symmetrical alkyne or alkene.
- Comparing with a known sample's IR spectrum confirms the identity of the compound.

Worked Example: Write the approximate absorption in IR for each of the compounds given below.



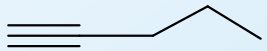
1

~1700 cm^{-1}



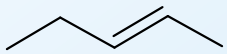
2

C=O: ~1700 cm^{-1}
N-H: ~3300 (2 peaks) cm^{-1}



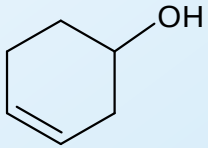
3

C≡C ~2100 cm^{-1}
≡ C-H: ~3300 cm^{-1}



5

C=C ~1620 cm^{-1}
=C-H ~3010 cm^{-1}

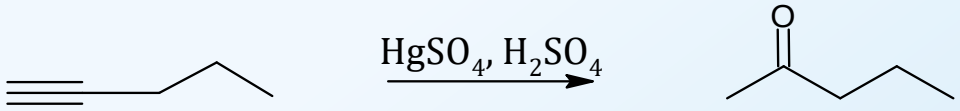


6

OH ~3500 cm^{-1}
C=C ~1620 cm^{-1}
=C-H ~3010 cm^{-1}

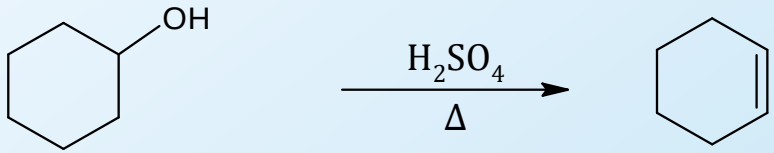
Worked Example: What changeds in IR will you see in the following reaction?

a



Peaks for C≡C ~2100 cm^{-1} and ≡ C-H ~3300 cm^{-1} will disappear and one around 1700 cm^{-1} will appear.

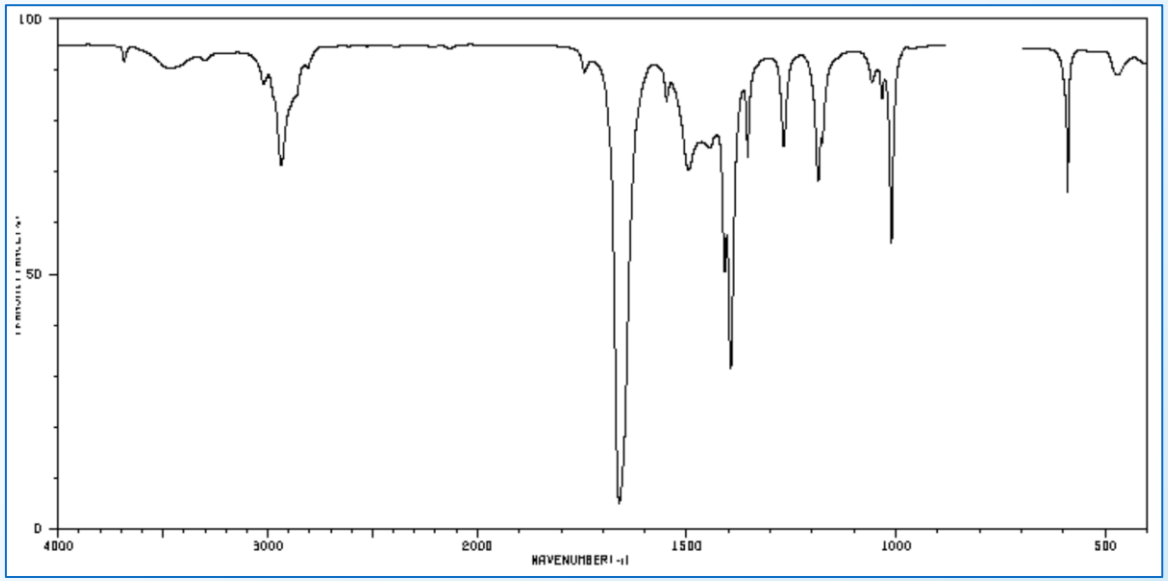
b

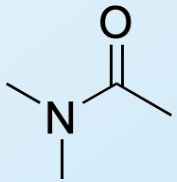


OH peak around 3500 cm^{-1} will disappear and peaks around 1600 cm^{-1} and 3100 cm^{-1} will appear.

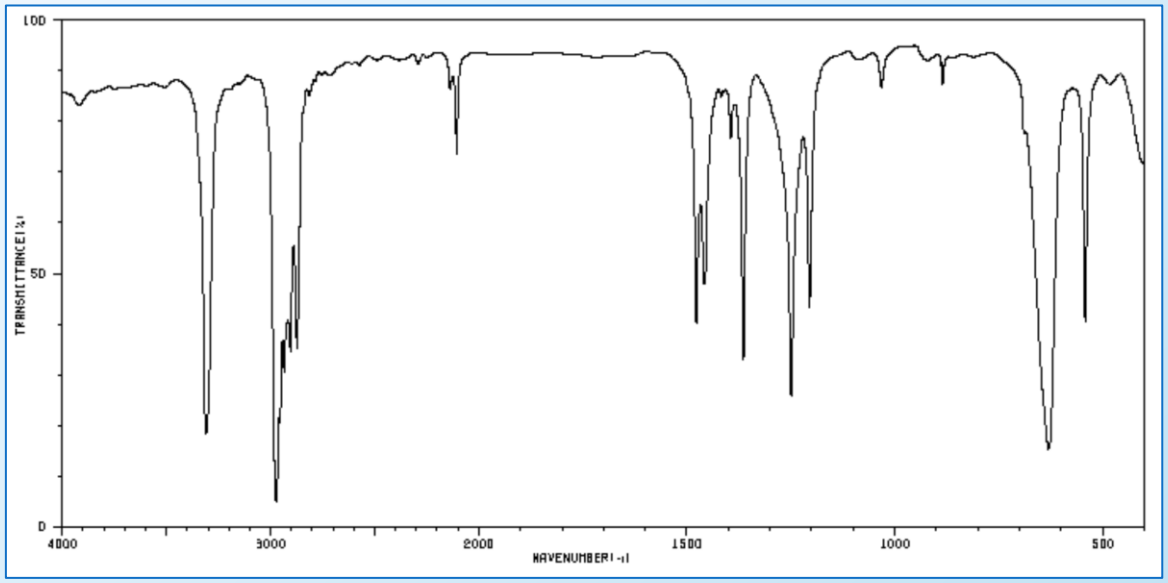
Worked Example: What functional groups might be present in the following IR spectra?

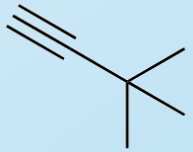
a





b





Key Concepts

- IR frequencies and relationship to functional group.