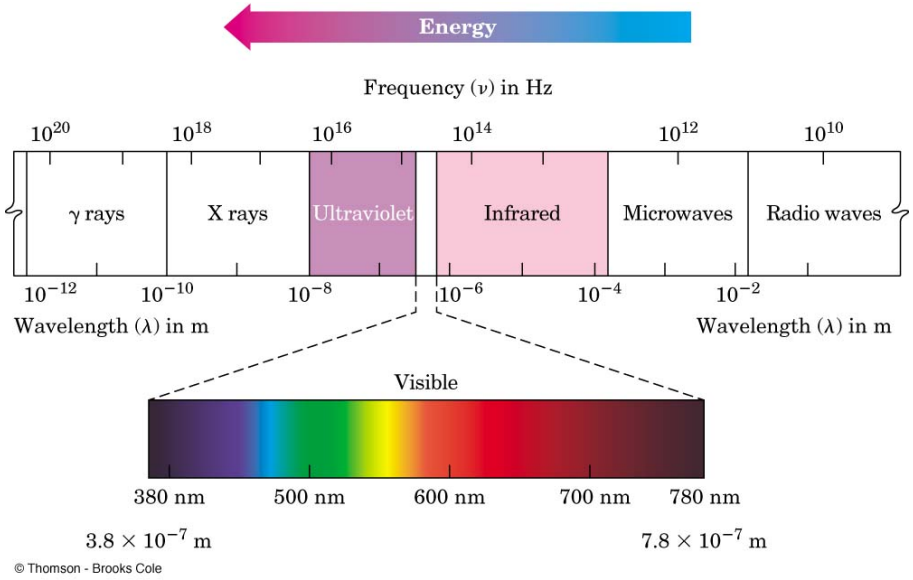
Determining the Structure of an Organic Compound

- The analysis of a reaction requires that we know the full structure of the products as well as the reactants.
- In the 19th and early 20th centuries, structures were determined by synthesis and chemical degradation that related compounds to each other.
- Physical methods now permit structures to be determined directly. Today, we will examine:
  - infrared (IR) spectroscopy

Spectroscopy of the Electromagnetic Spectrum

- Radiant energy is proportional to its frequency (cycles/s = Hz) as a wave (Amplitude is its height)
- Different types are classified by frequency or wavelength ranges



Absorption Spectra

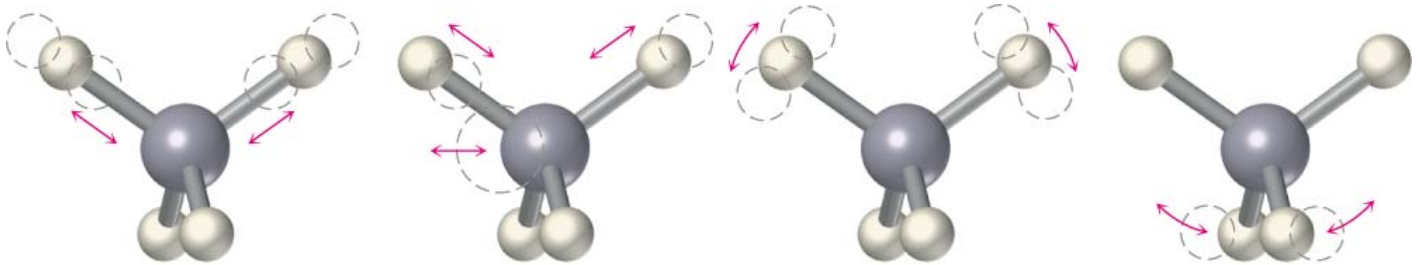
- Organic compound exposed to electromagnetic radiation, can absorb energy of only certain wavelengths (unit of energy)
  - Transmits energy of other wavelengths.
- Changing wavelengths to determine which are absorbed and which are transmitted produces an **absorption spectrum.**
- Absorbed energy is distributed (expended) internally in a distinct and reproducible way.

Infrared Spectroscopy of Organic Molecules

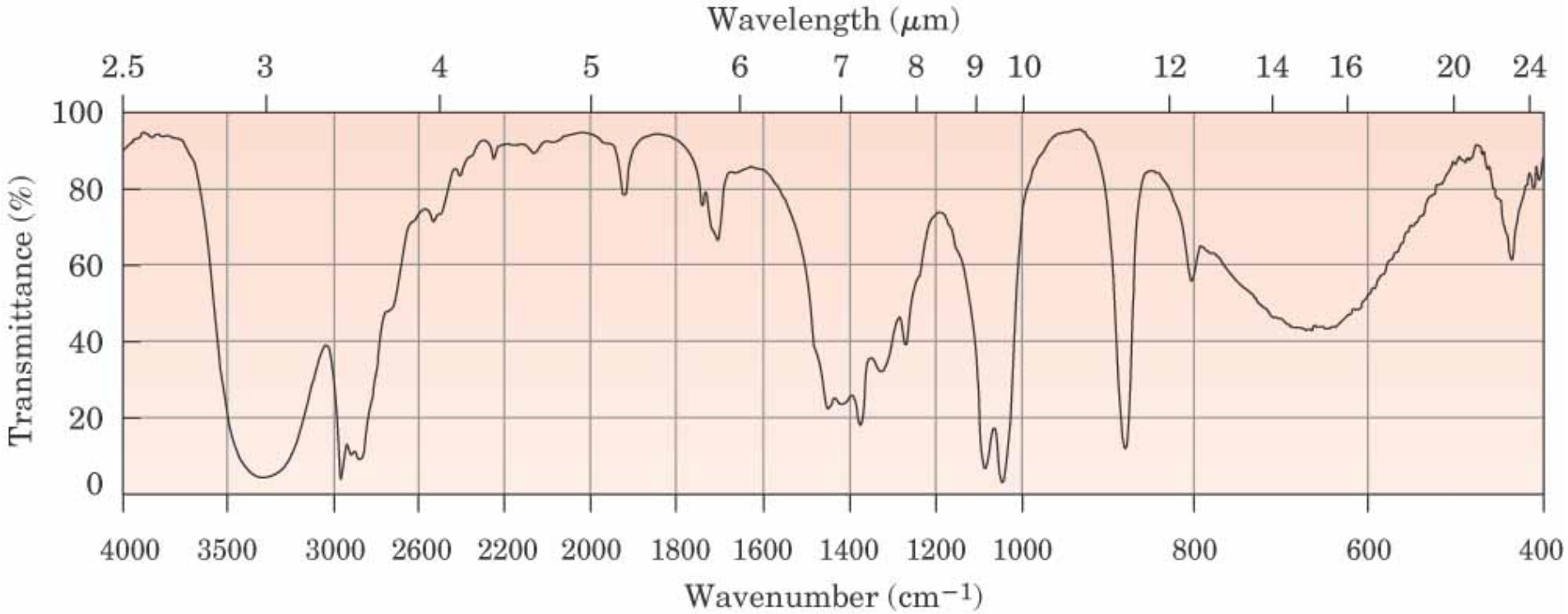
- IR region lower energy than visible light (below red – produces heating as with a heat lamp at the Blue Wall)
- 2.5×10^{-6} m to 2.5×10^{-5} m region used by organic chemists for structural analysis
- IR energy in a spectrum is usually measured as wavenumber (cm^{-1}), the inverse of wavelength and proportional to frequency
- Specific IR absorbed by organic molecule related to its structure

Infrared Energy Modes

- IR energy absorption corresponds to specific modes, corresponding to combinations of atomic movements, such as bending and stretching of bonds between groups of atoms called “normal modes”
- Energy is characteristic of the atoms in the group and their bonding
- Corresponds to vibrations and rotations



The resulting spectrum…



Sample preparation….

Thin film – salt plates

KBr discs – high pressure

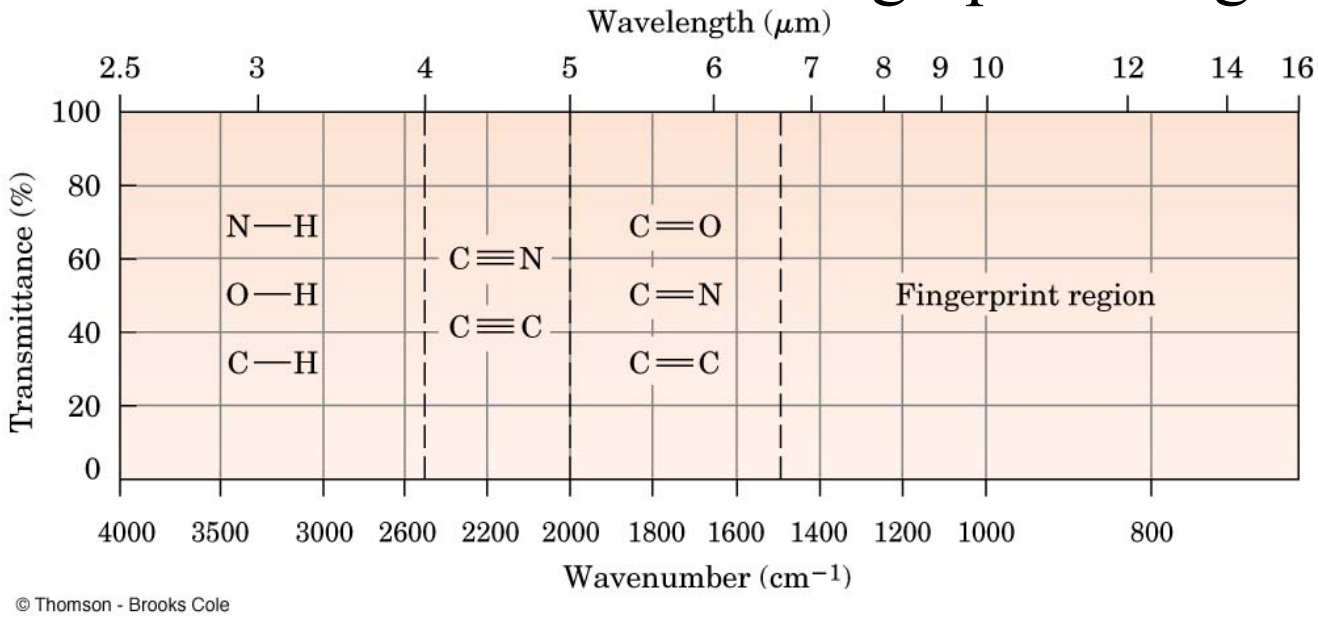
Anyone used other methods?

Interpreting Infrared Spectra

- Most functional groups absorb at about the same energy and intensity **independent** of the molecule they are in.
- Characteristic higher energy IR absorptions can be used to confirm the existence or the presence of a functional group in a molecule.
- IR spectrum has lower energy region characteristic of molecule as a whole ("fingerprint" region).

Regions of the Infrared Spectrum

- 4000-2500 cm^{-1} N-H, C-H, O-H (stretching)
  - 3300-3600 N-H, O-H
  - 3000 C-H
- 2500-2000 cm^{-1} C≡C and C ≡ N (stretching)
- 2000-1500 cm^{-1} double bonds (stretching)
  - C=O 1680-1750
  - C=C 1640-1680 cm^{-1}
- Below 1500 cm^{-1} "fingerprint" region

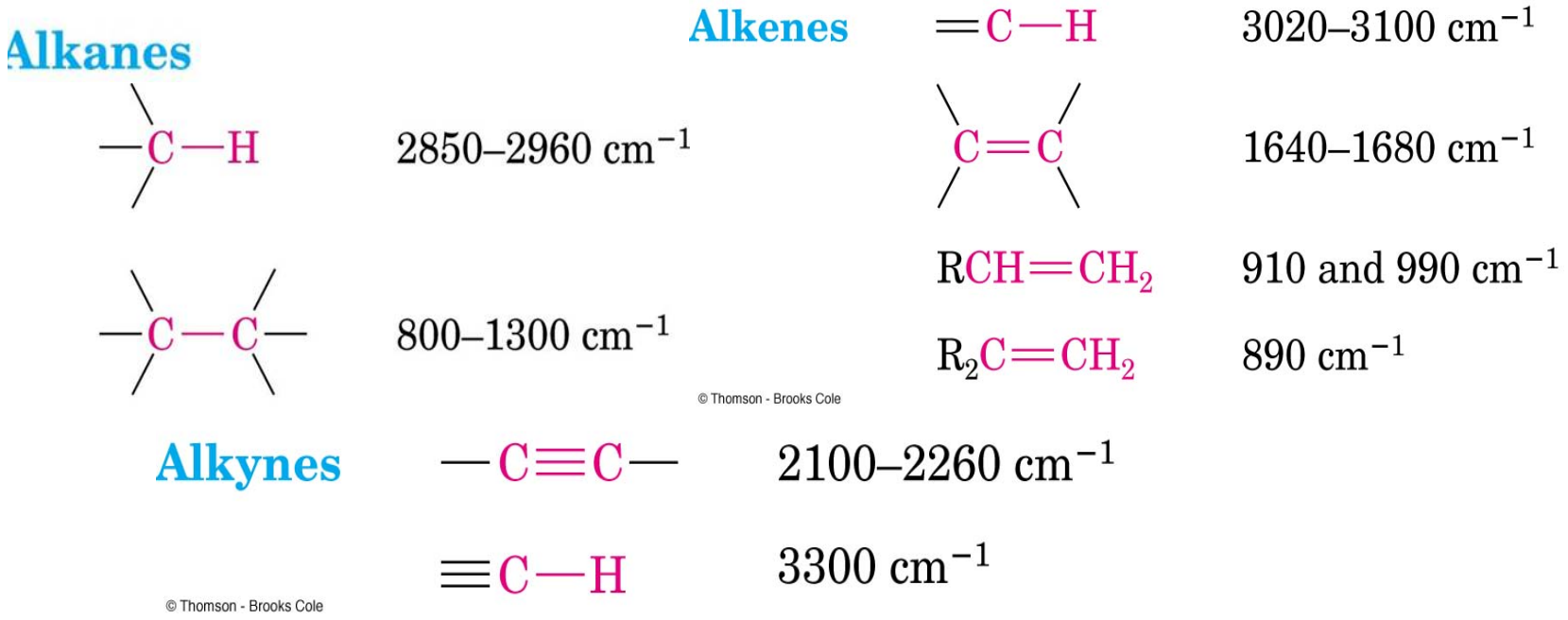


Differences in Infrared Absorptions

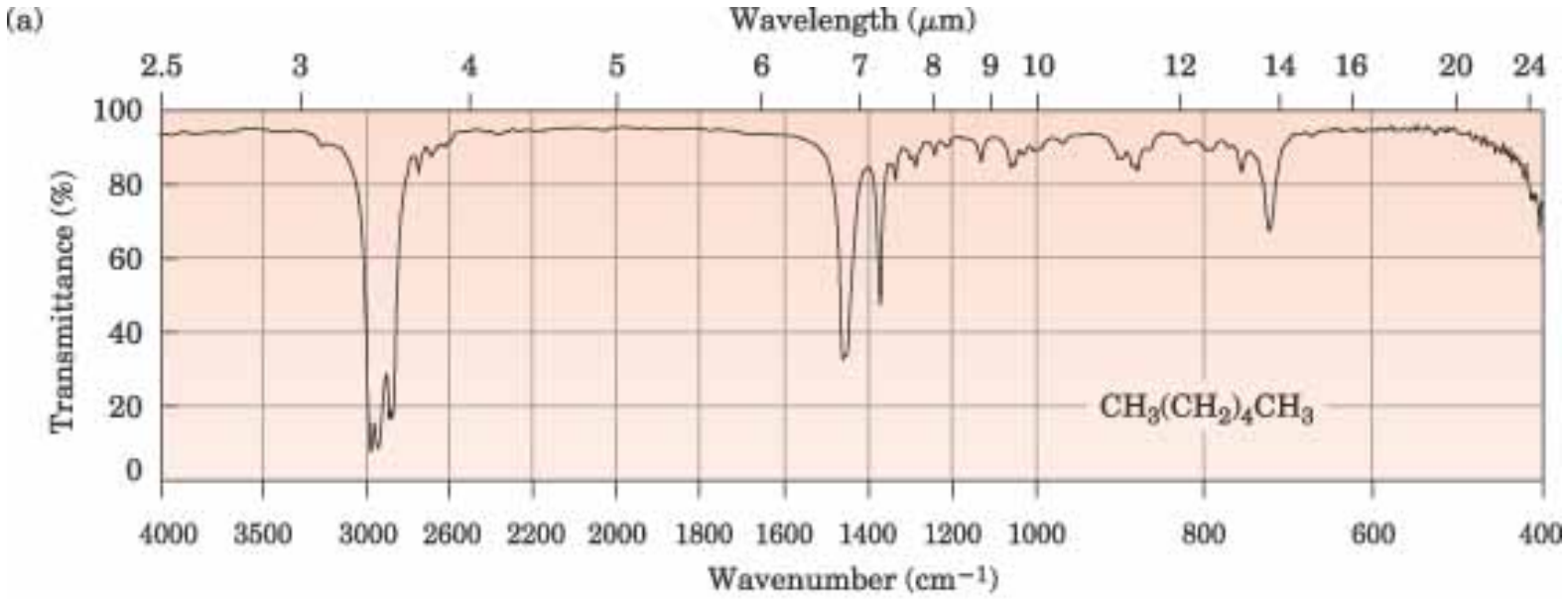
- Molecules vibrate and rotate in normal modes, which are **combinations** of motions (related to force constants).
- Bond stretching dominates higher energy modes.
- Light objects connected to heavy objects vibrate fastest: C-H, N-H, O-H
- For two heavy atoms, stronger bond requires more energy: alkyne, nitrile > C=C, C=O, C=N > C-C, C-O, C-N, C-halogen

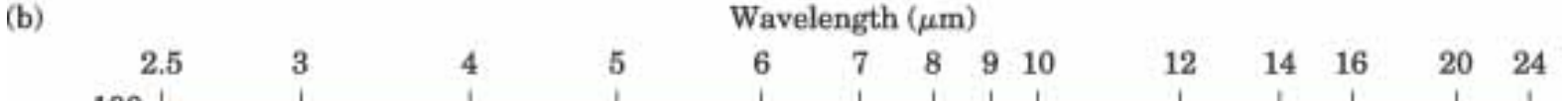
Infrared Spectra of Hydrocarbons

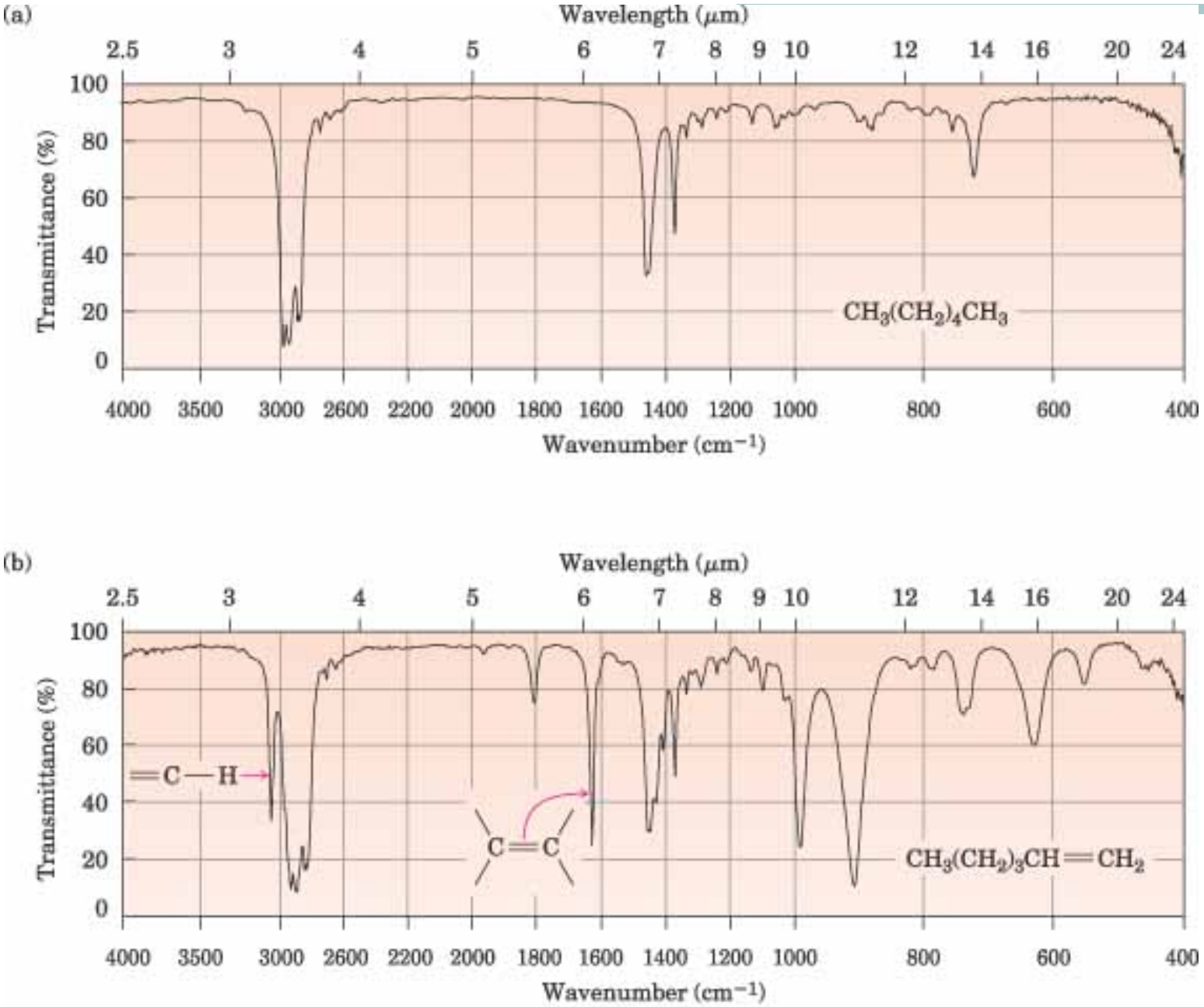
- C-H, C-C, C=C, C ≡ C have characteristic peaks
  - absence helps rule out C=C or C ≡ C

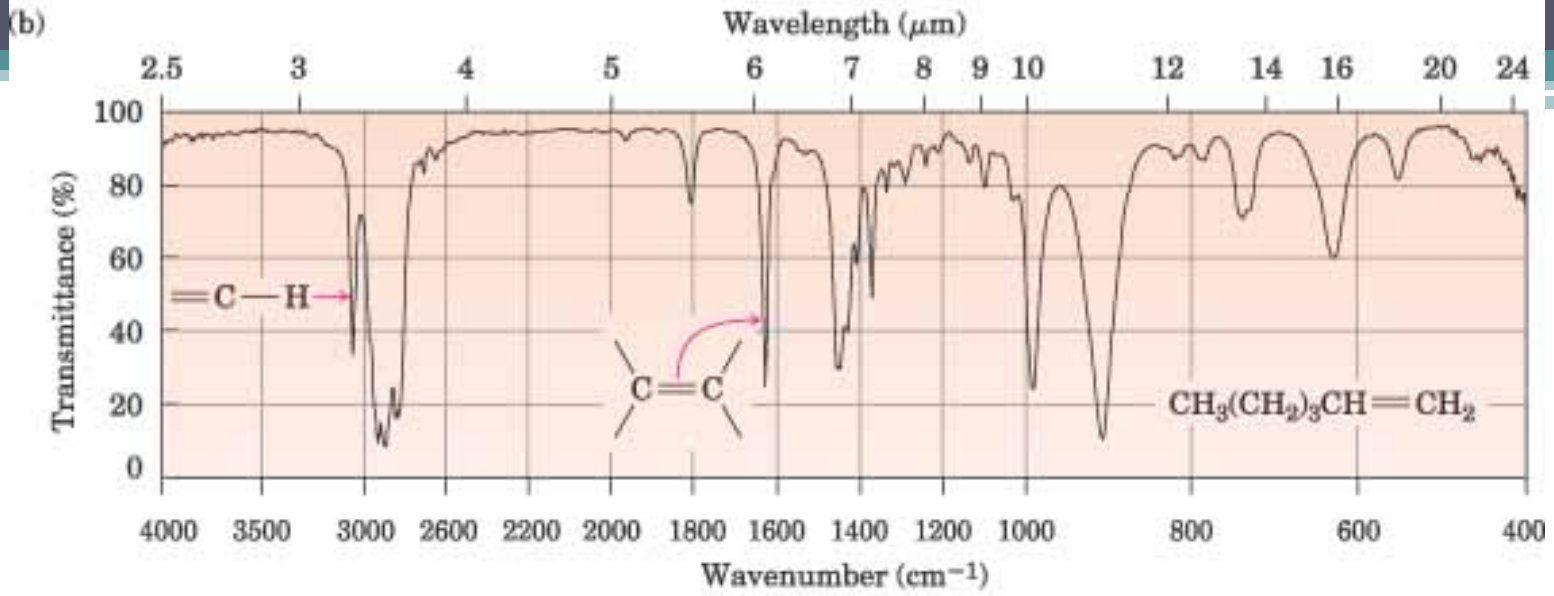


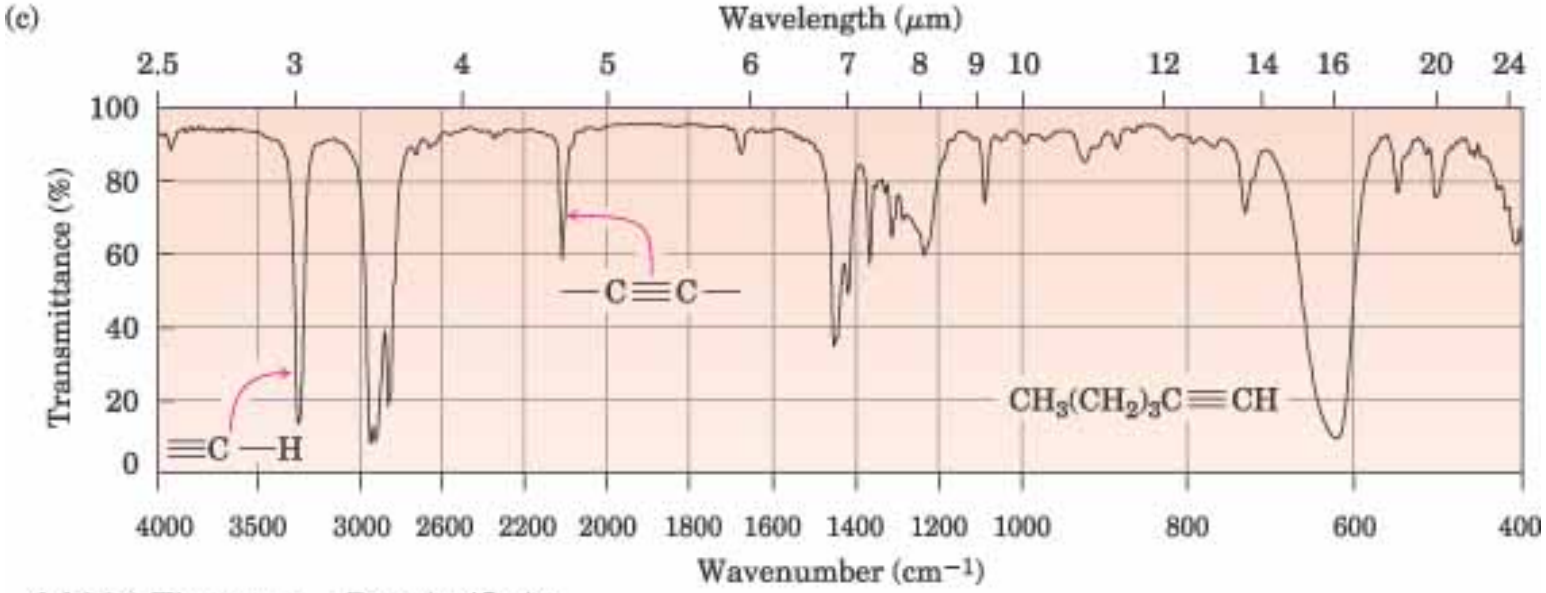
© Thomson - Brooks Cole


(a)
Wavelength (μm)
2.5
3
4
5
6
7
8
9
10
12
14
16
20
24
100
80
60
40
20
0
Transmittance (%)
CH3(CH2)4CH3
4000
3500
3000
2600
2200
2000
1800
1600
1400
1200
1000
800
600
400
Wavenumber (cm−1)


(b)
Wavelength (μm)
2.5
3
4
5
6
7
8
9
10
12
14
16
20
24


(a)
Wavelength (μm)
2.5 3 4 5 6 7 8 9 10 12 14 16 20 24
Transmittance (%)
100 80 60 40 20 0
CH3(CH2)4CH3
4000 3500 3000 2600 2200 2000 1800 1600 1400 1200 1000 800 600 400
Wavenumber (cm−1)
(b)
Wavelength (μm)
2.5 3 4 5 6 7 8 9 10 12 14 16 20 24
Transmittance (%)
100 80 60 40 20 0
=C—H
C=C
CH3(CH2)3CH=CH2
4000 3500 3000 2600 2200 2000 1800 1600 1400 1200 1000 800 600 400
Wavenumber (cm−1)



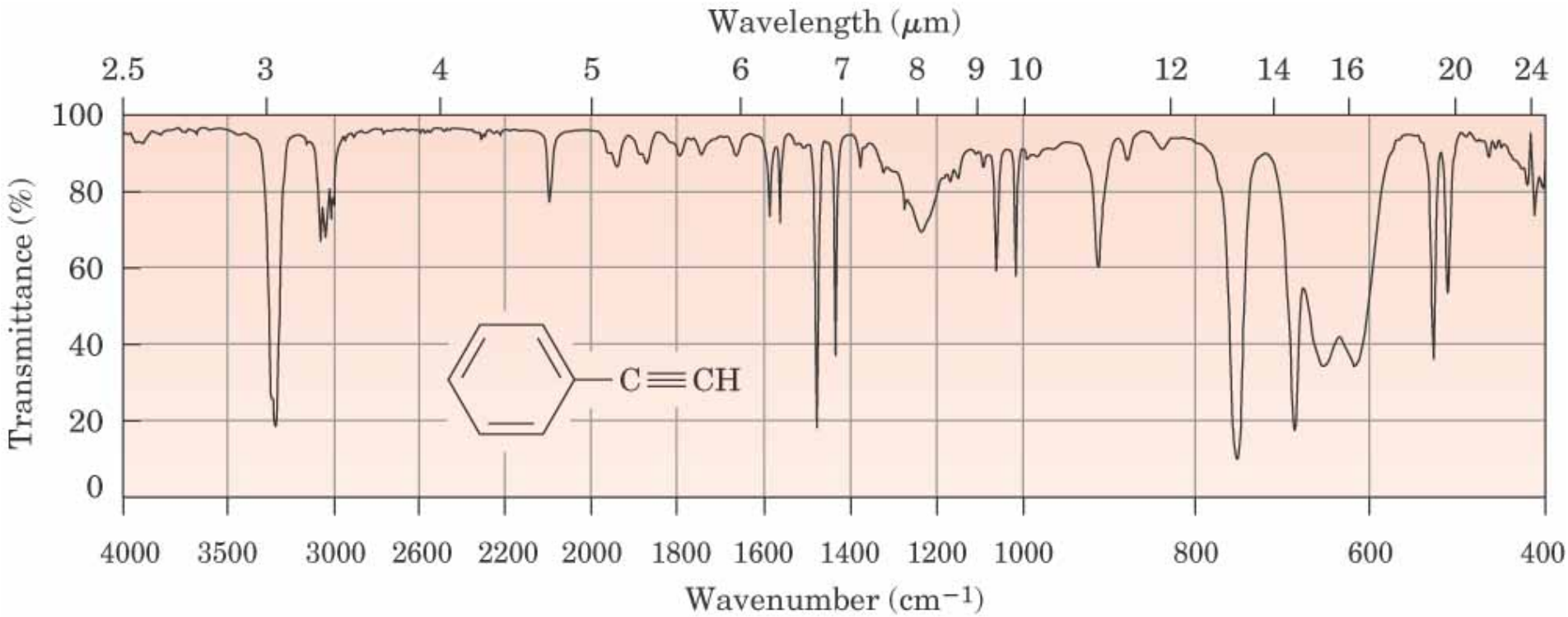


IR: Aromatic Compounds

- Weak C–H stretch at 3030 cm^{-1}
- Weak absorptions 1660 - 2000 cm^{-1} range
- Medium-intensity absorptions 1450 to 1600 cm^{-1}
- See spectrum of phenylacetylene – next slide

Aromatic compounds

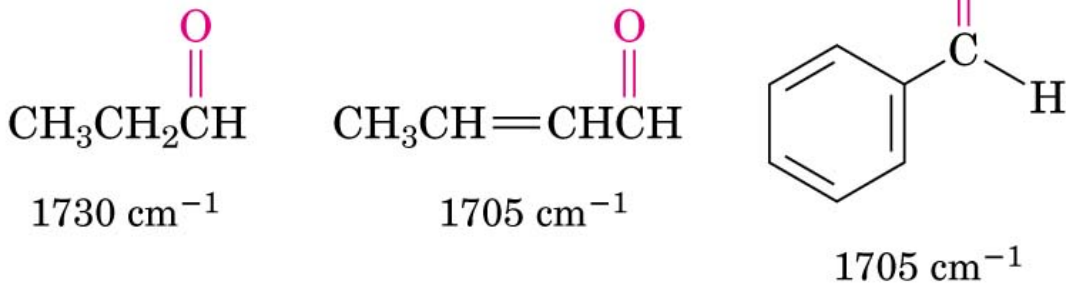
C–H	3030 cm^{-1} (weak)
Ring	1660–2000 cm^{-1} (weak) 1450–1600 cm^{-1} (medium)

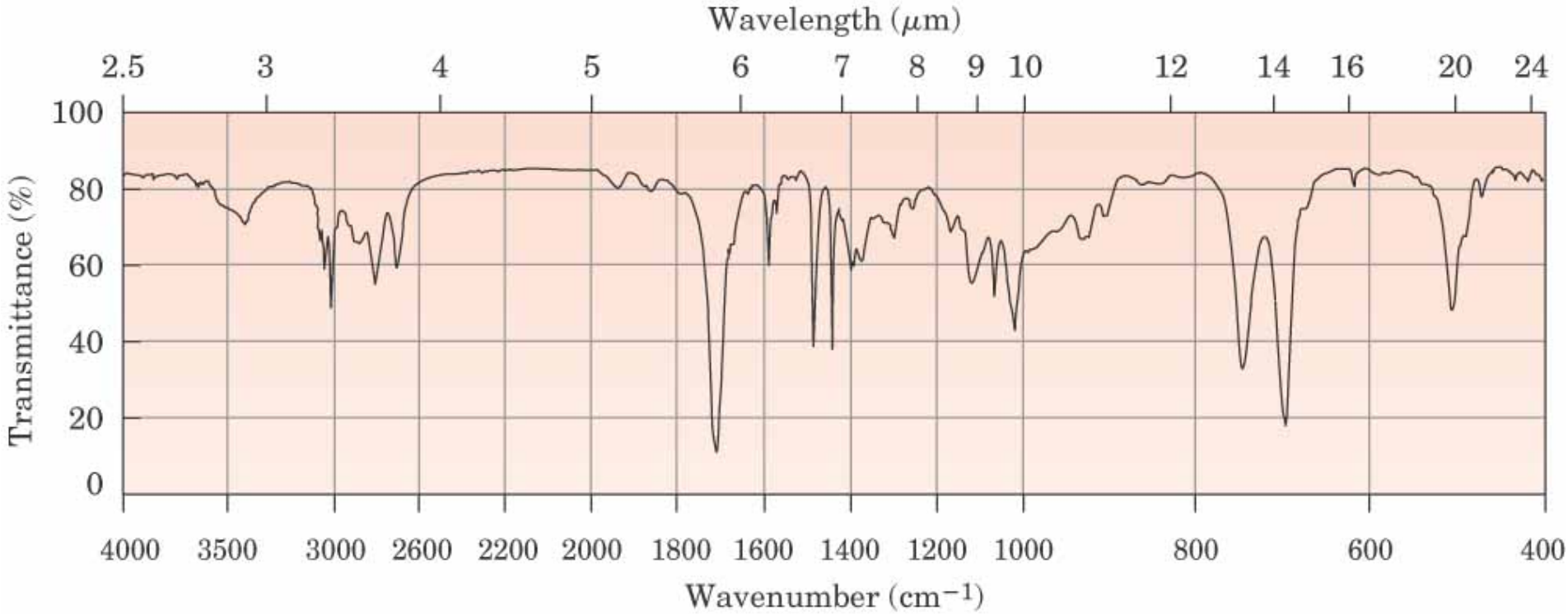


IR: Carbonyl Compounds

- Strong, sharp C=O peak 1670 to 1780 cm^{-1}
- Exact absorption characteristic of type of carbonyl compound
  - 1730 cm^{-1} in saturated aldehydes
  - 1705 cm^{-1} in aldehydes next to double bond or aromatic ring

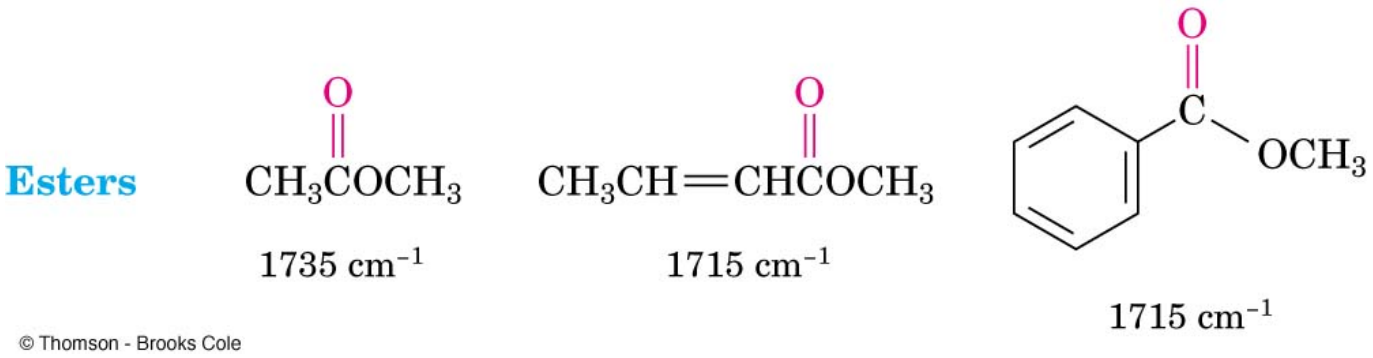
Aldehydes





C=O in Esters

- 1735 cm^{-1} in saturated esters
- 1715 cm^{-1} in esters next to aromatic ring or a double bond



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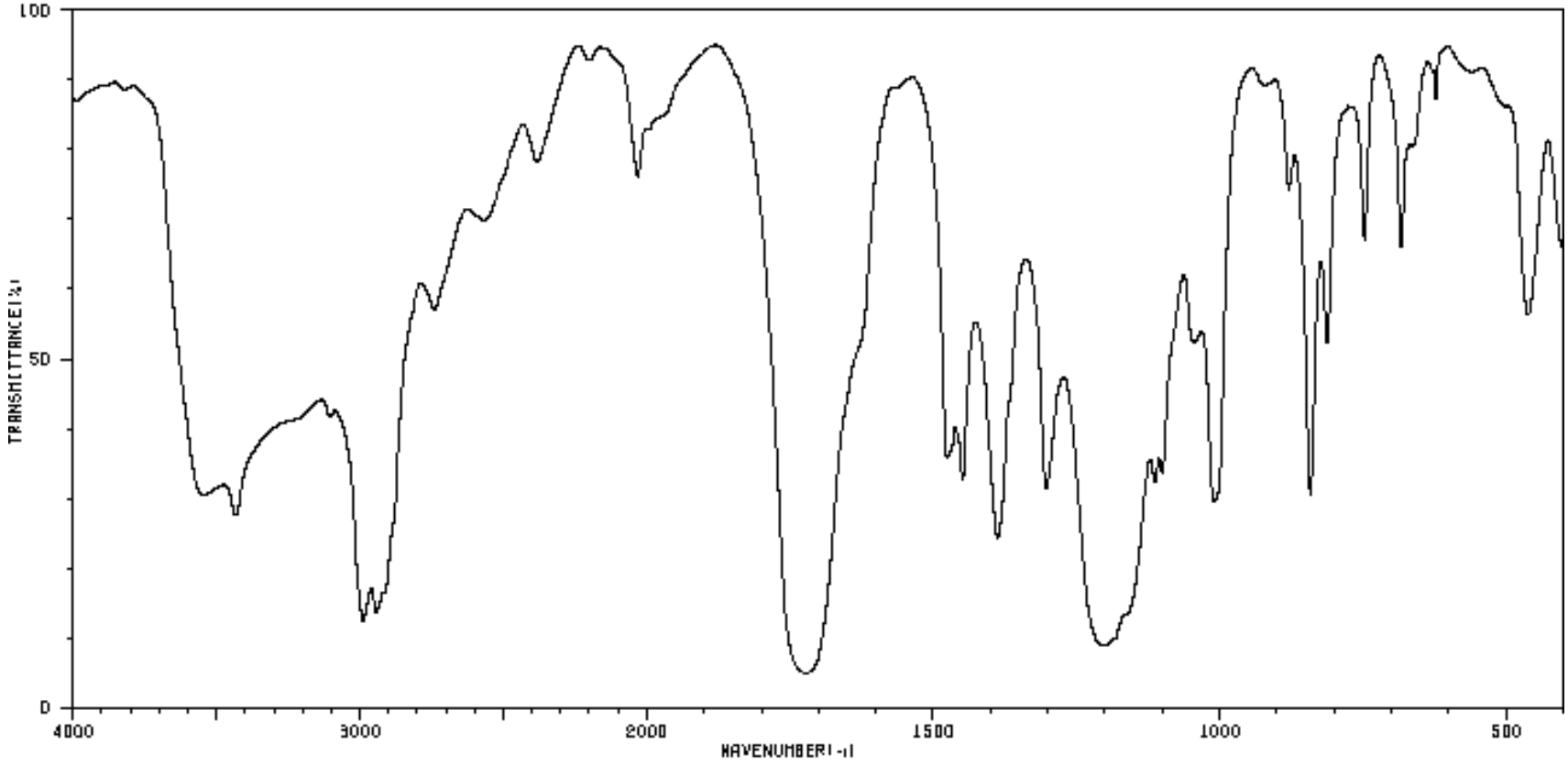
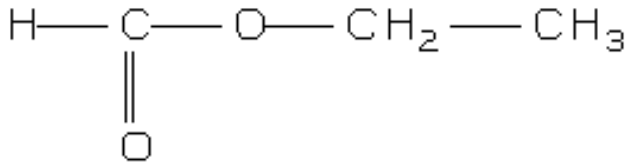
ETHYL FORMATE

$C_3H_6O_2$



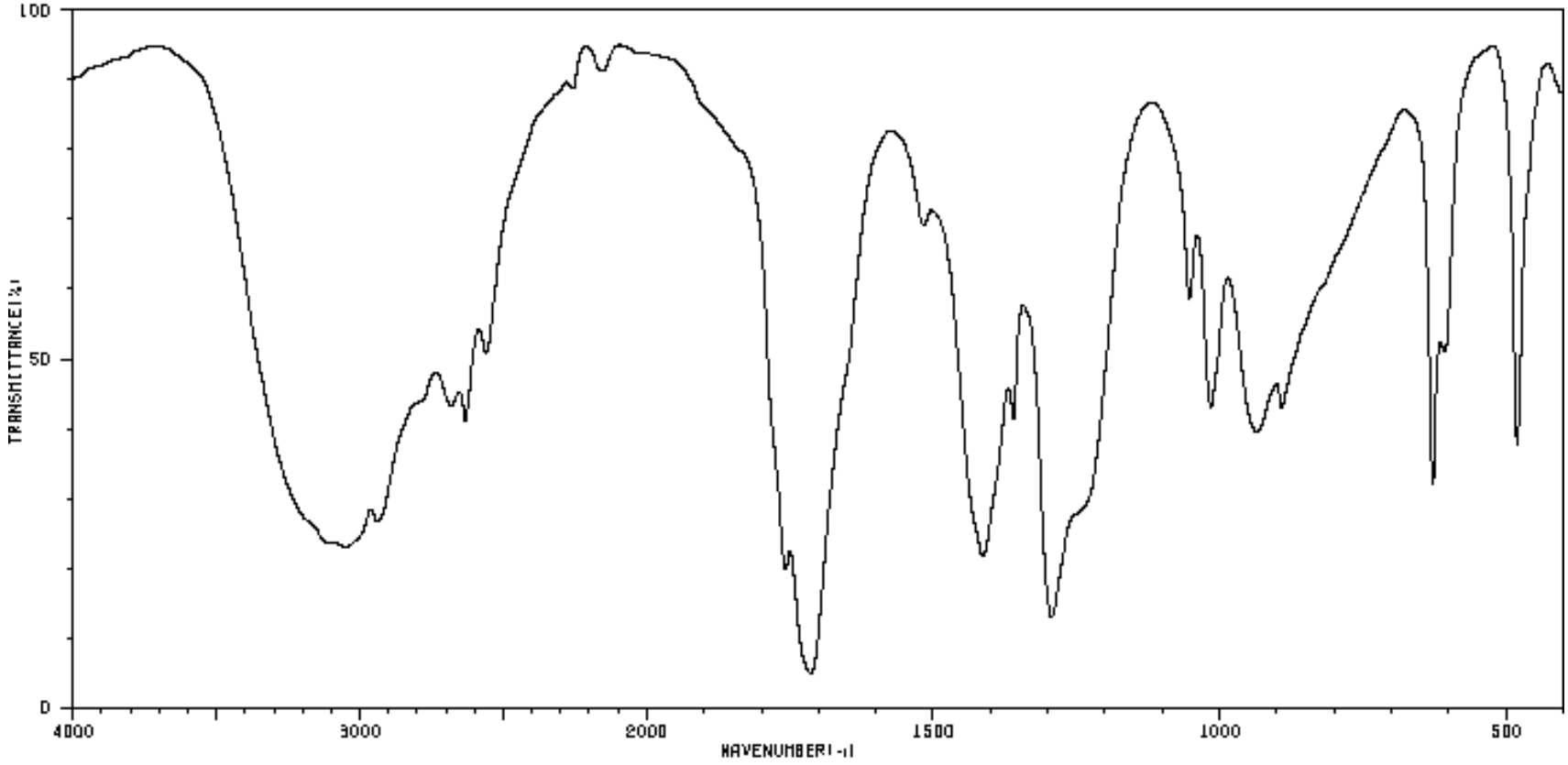
3646	29	2030	72	1206	8	880	70	462	63
3432	26	1726	4	1200	8	842	29		
2987	12	1721	4	1113	31	813	50		
2943	13	1477	34	1100	32	748	64		
2739	55	1449	31	1043	50	684	64		
2567	68	1388	29	1010	28	668	77		
2383	74	1303	30	920	86	623	84		



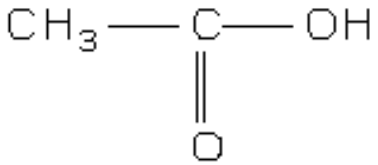
HIT-NO=950	SCORE= ( )	SDBS-NO=306	IR-NIDA-60820 : LIQUID FILM

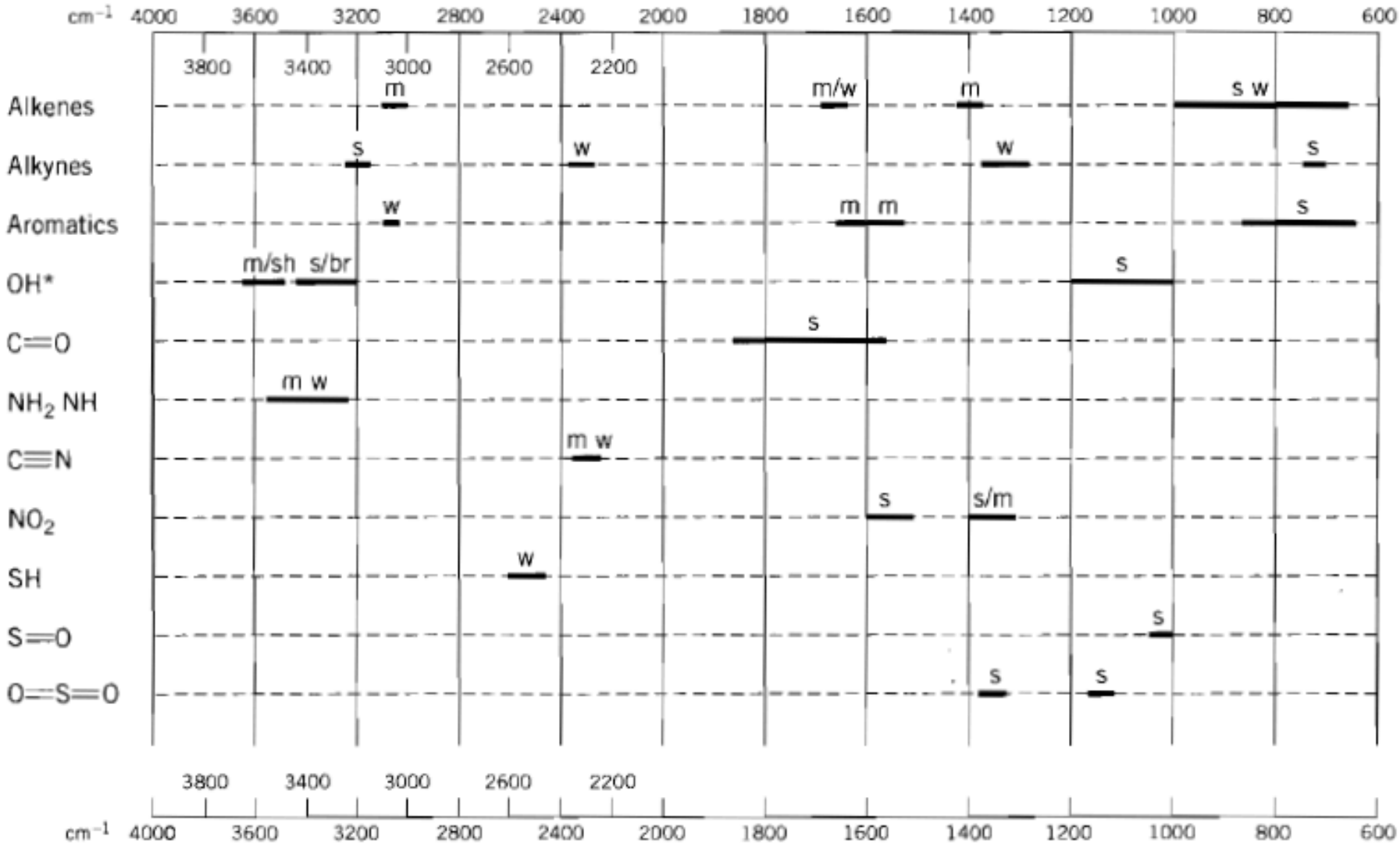
ACETIC ACID

$C_2H_4O_2$



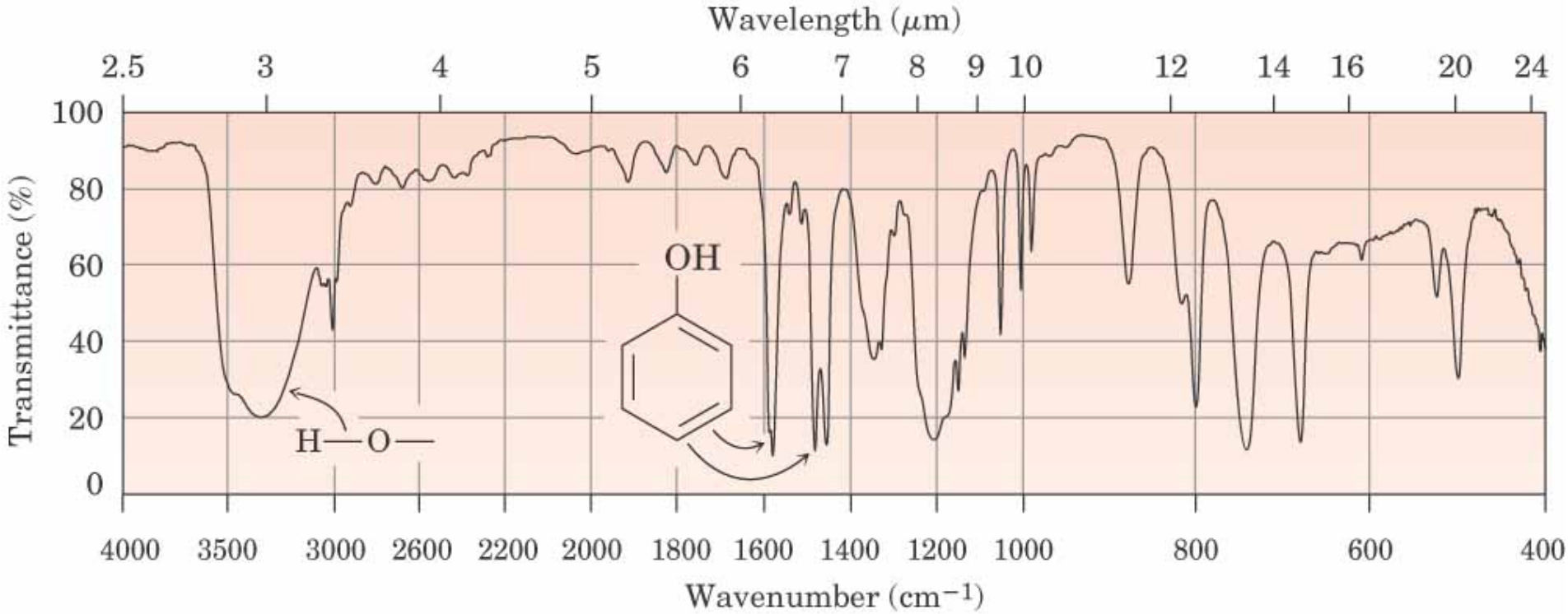
2937	26	1414	20	629	31
2684	41	1360	39	607	49
2631	39	1294	12	481	36
2669	49	1063	67	473	62
1758	19	1016	41		
1714	4	935	37		
1617	66	892	41		





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

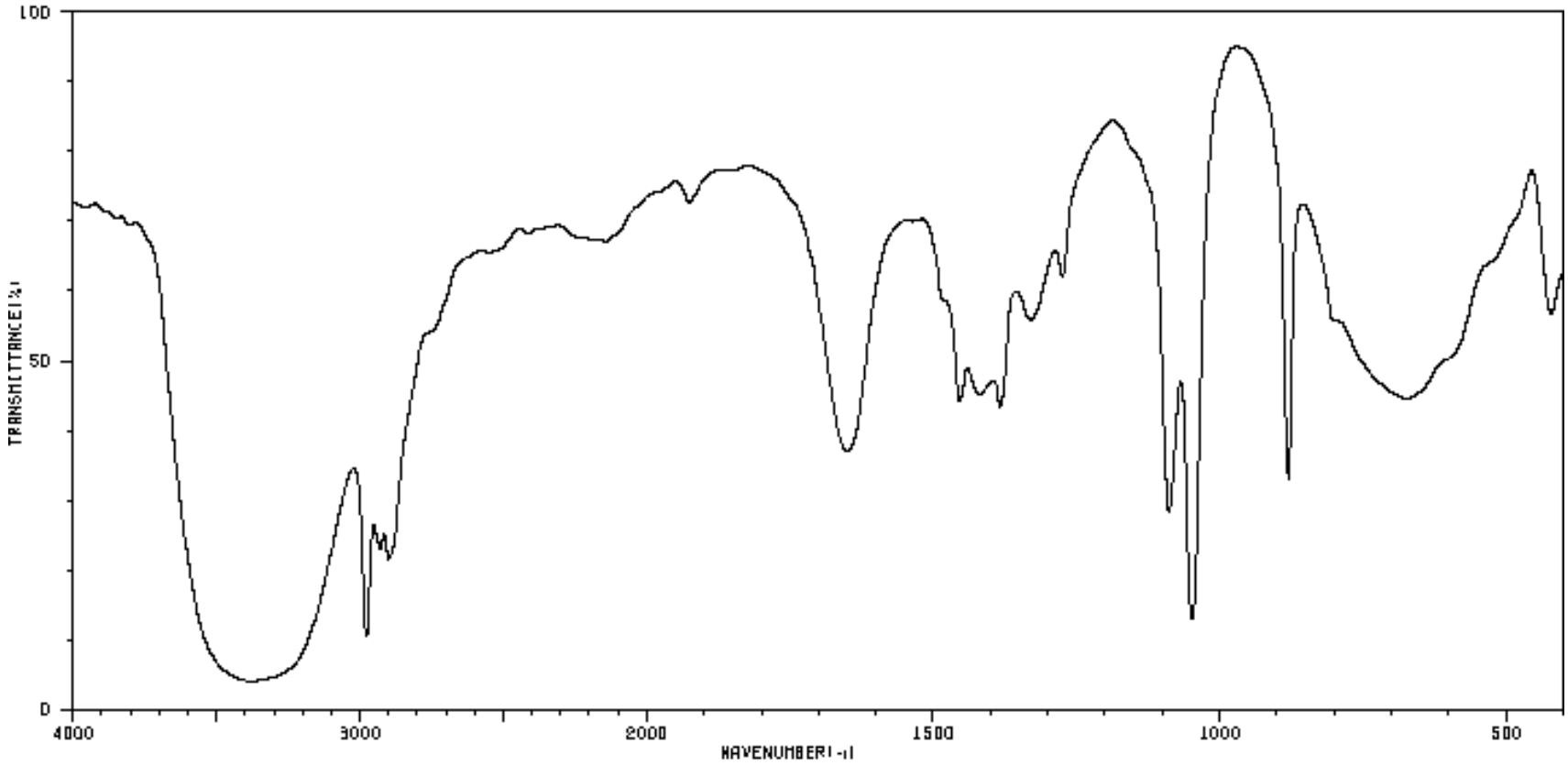
FIGURE 2.7. Simplified chart of several common functional groups with very characteristic absorptions. s = strong, m = medium, w = weak, sh = sharp, br = broad.



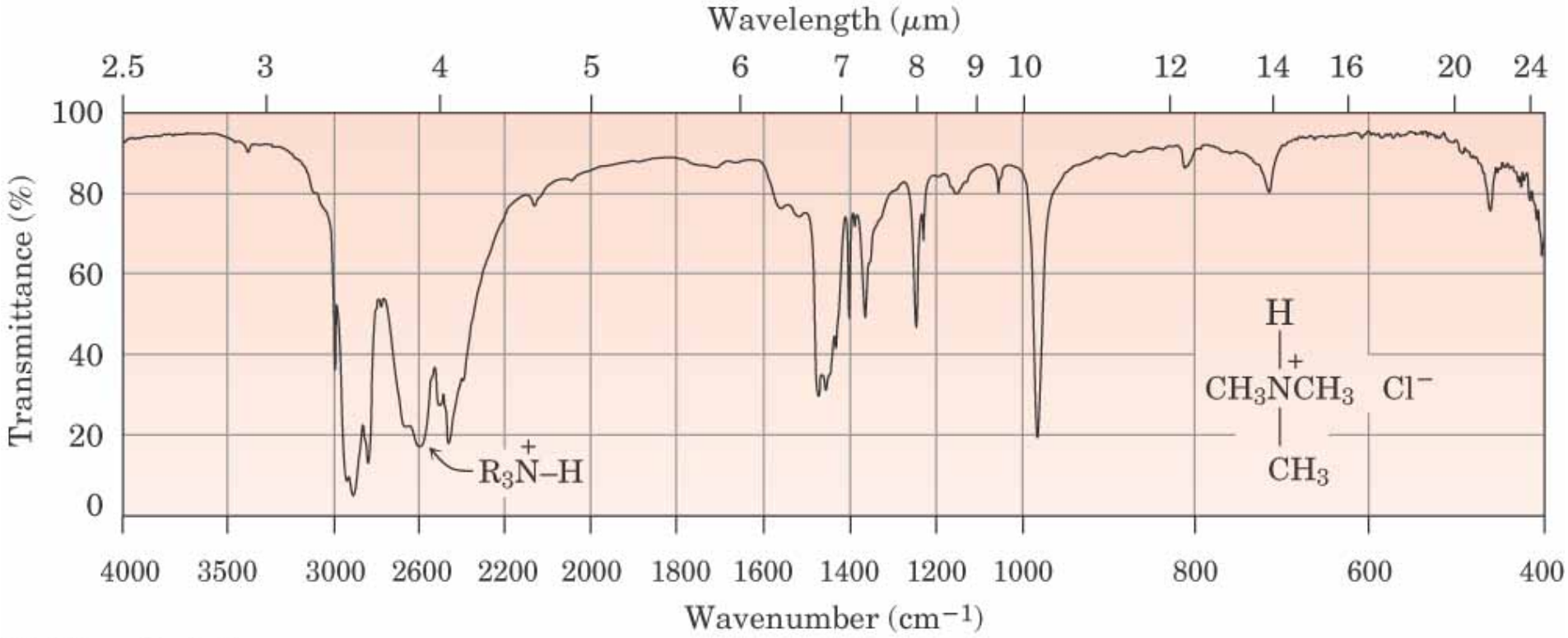
HIT-NO=1374	SCORE= ( )	SDBS-NO=1300	IR-NIDA-21941 : LIQUID FILM

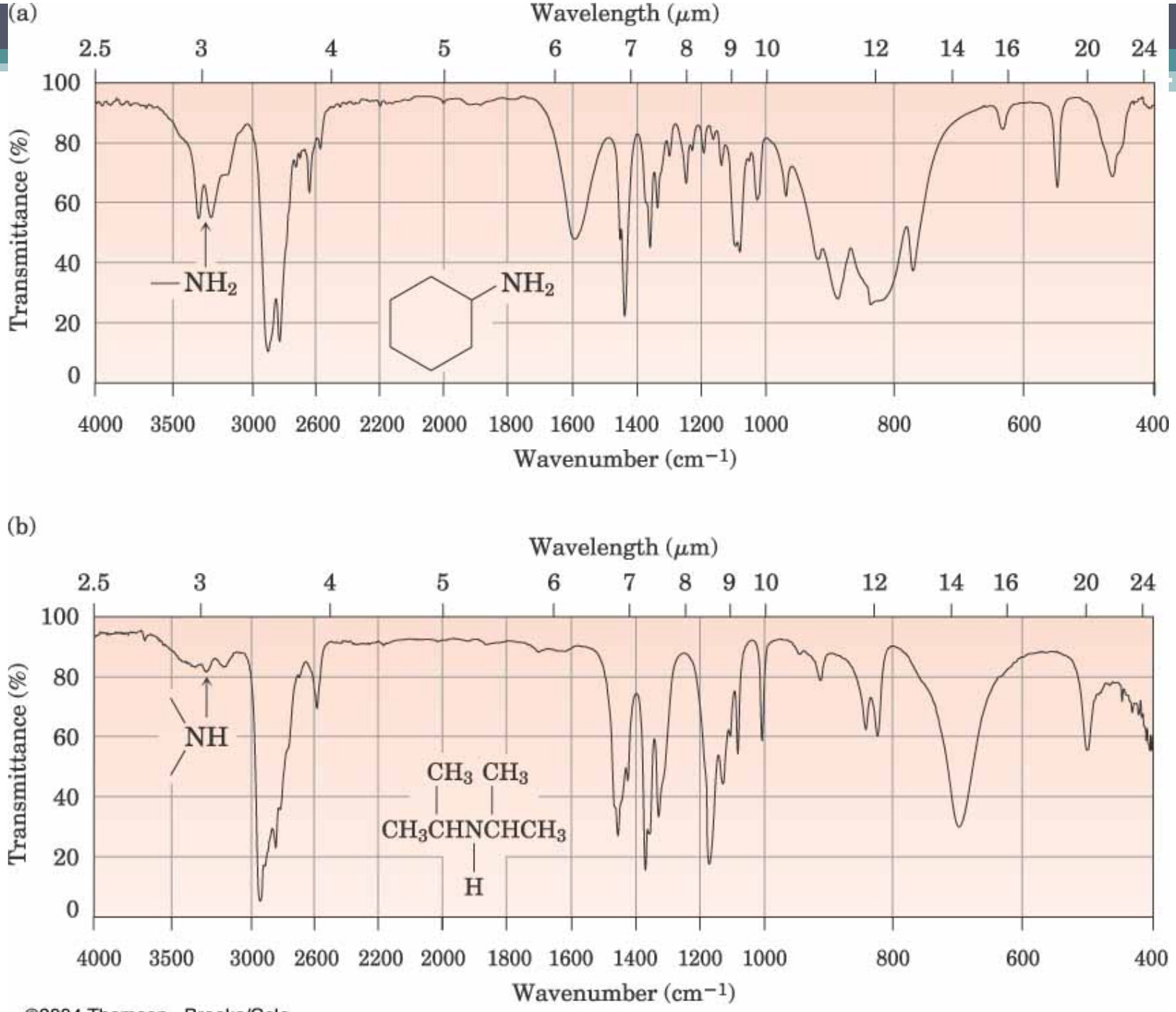
ETHYL ALCOHOL

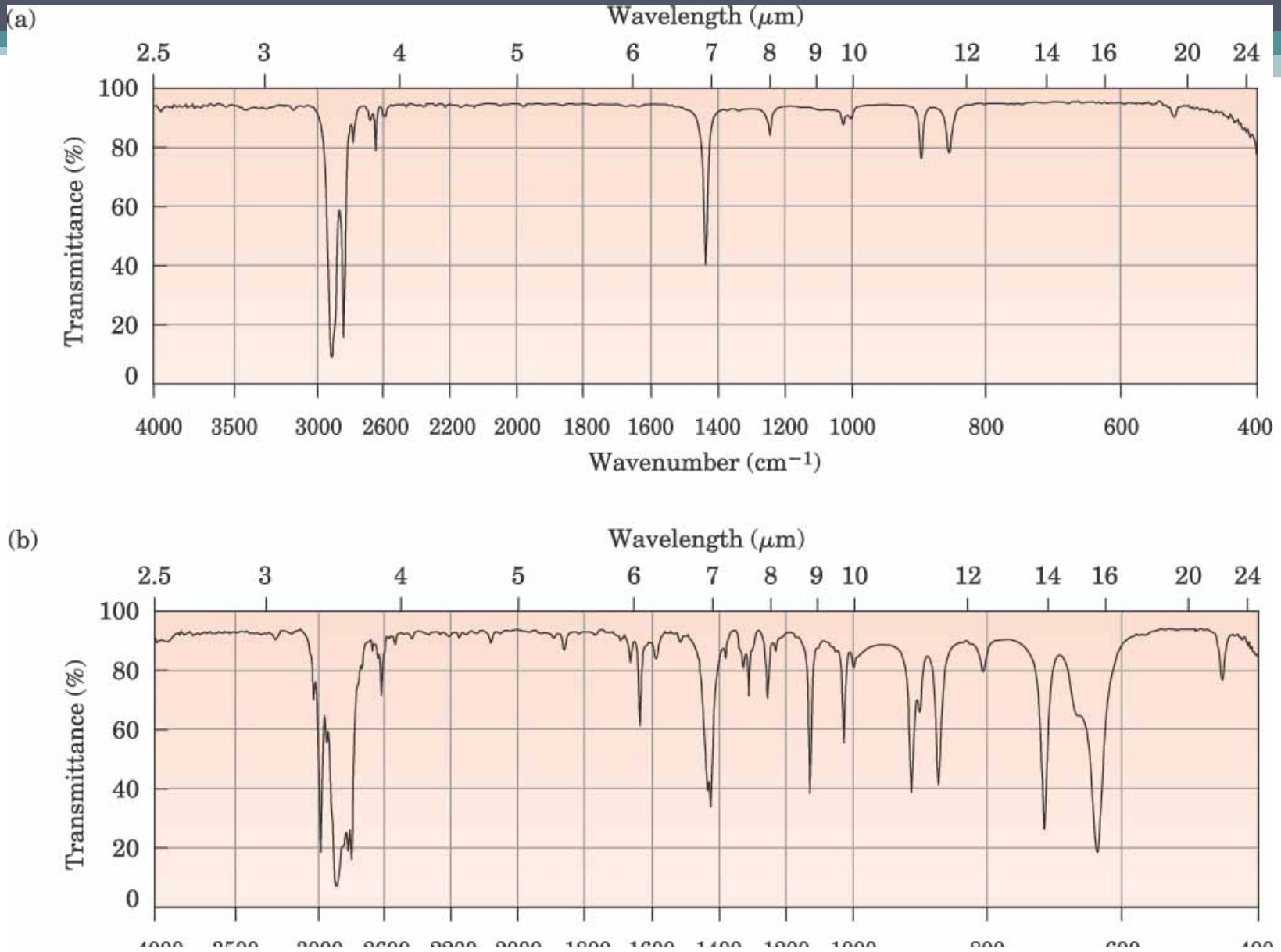
C_2H_6O



2977	4	1384	32
2930	13	1329	44
2899	12	1275	52
1926	62	1089	18
1650	26	1048	6
1454	33	880	22
1418	33		

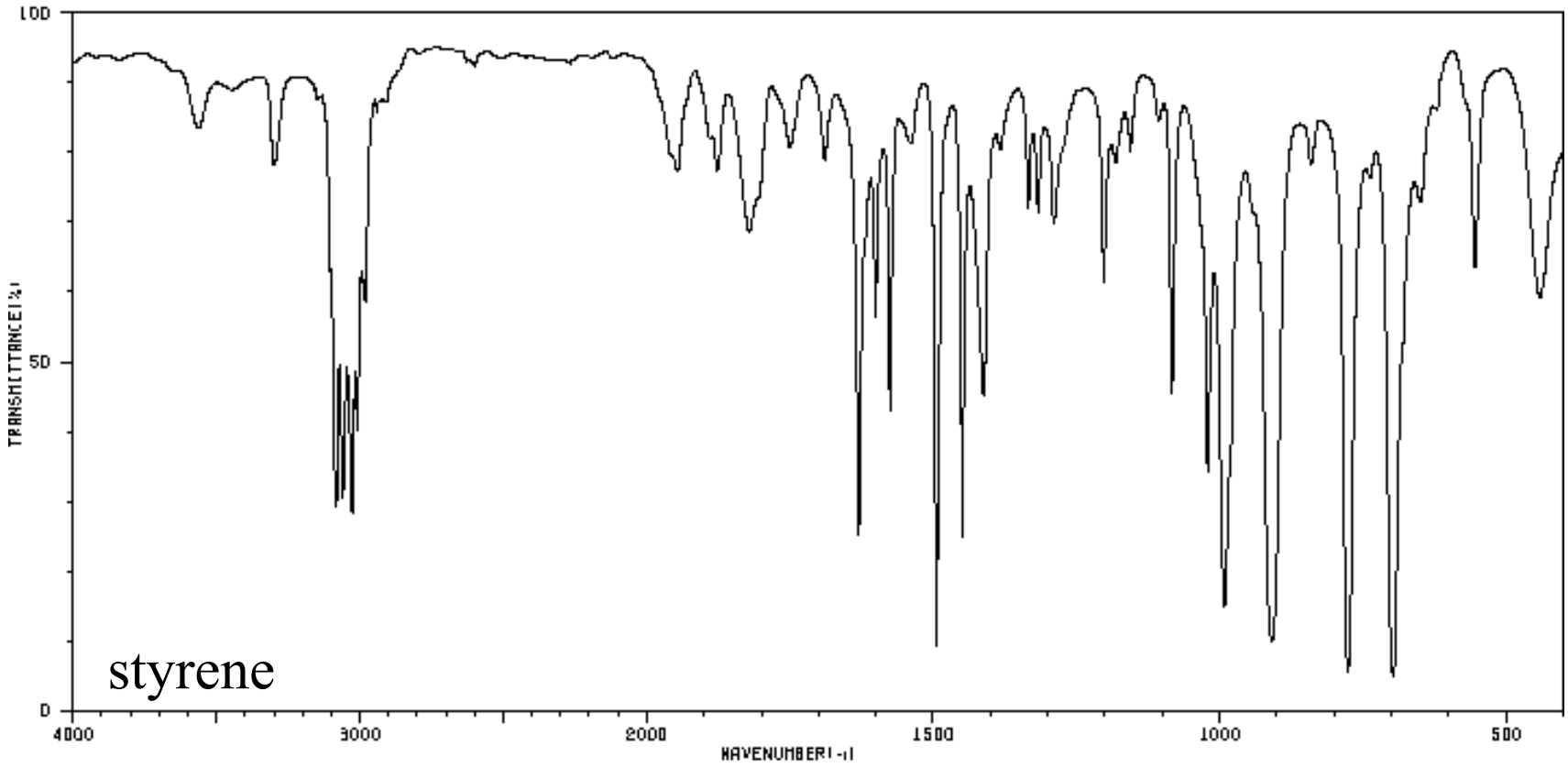


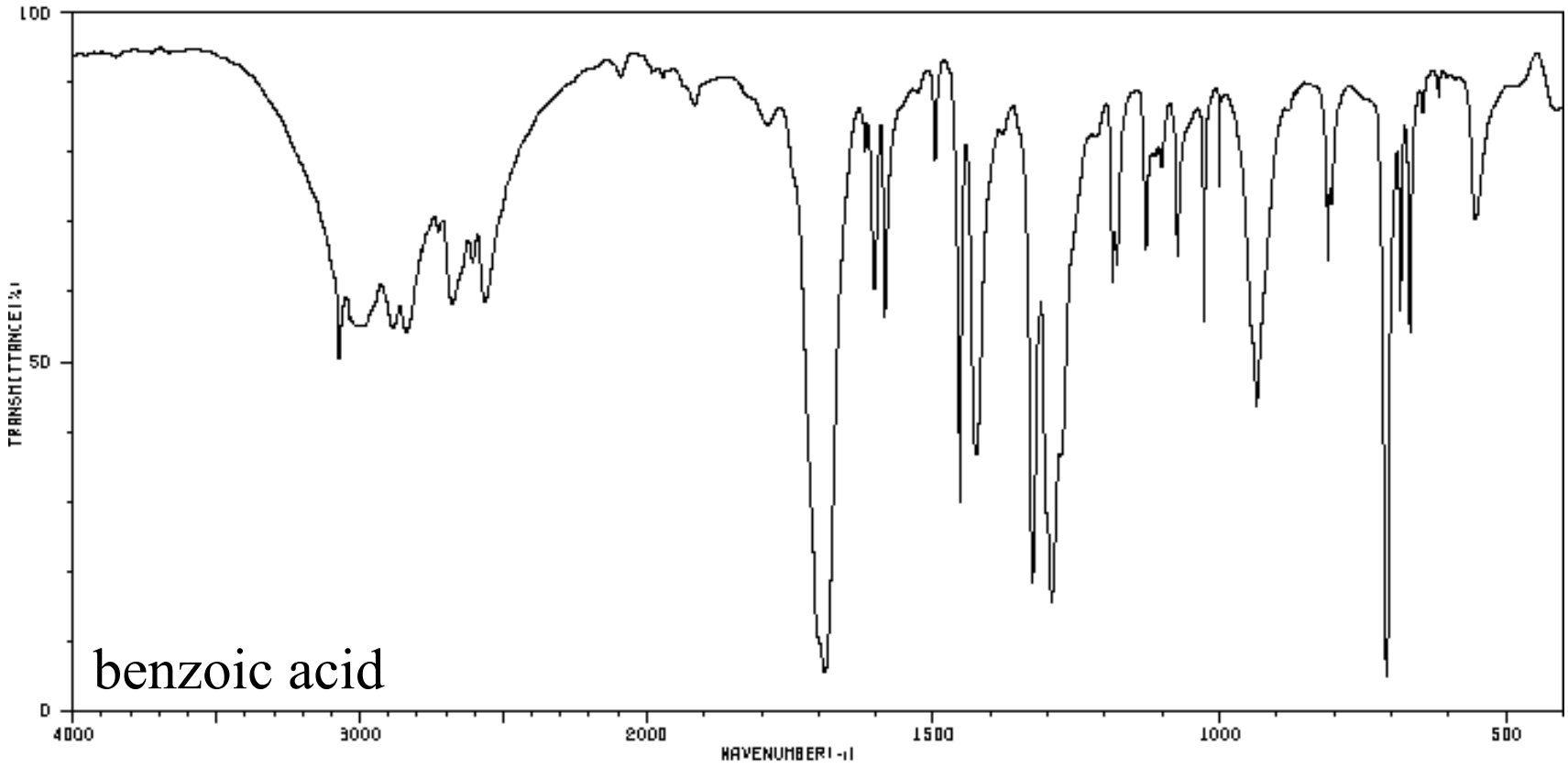




Cyclohexene, cyclohexane

Ok, participation time…..6 groups


100
50
0
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
styrene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0
TRANSMITTANCE[%]
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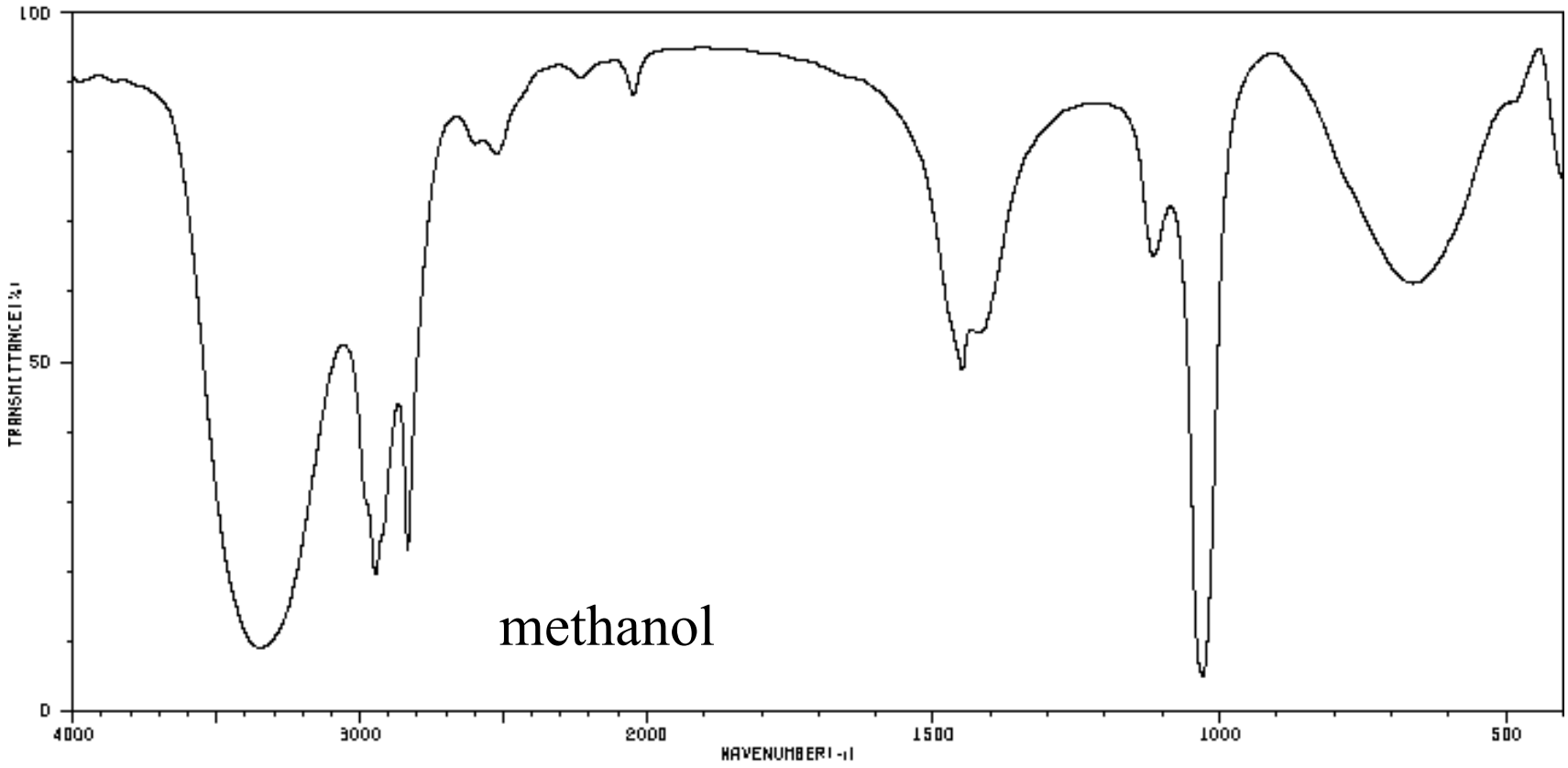
2000
1500
1000
500
WAVENUMBER[-1]
benzoic acid


100
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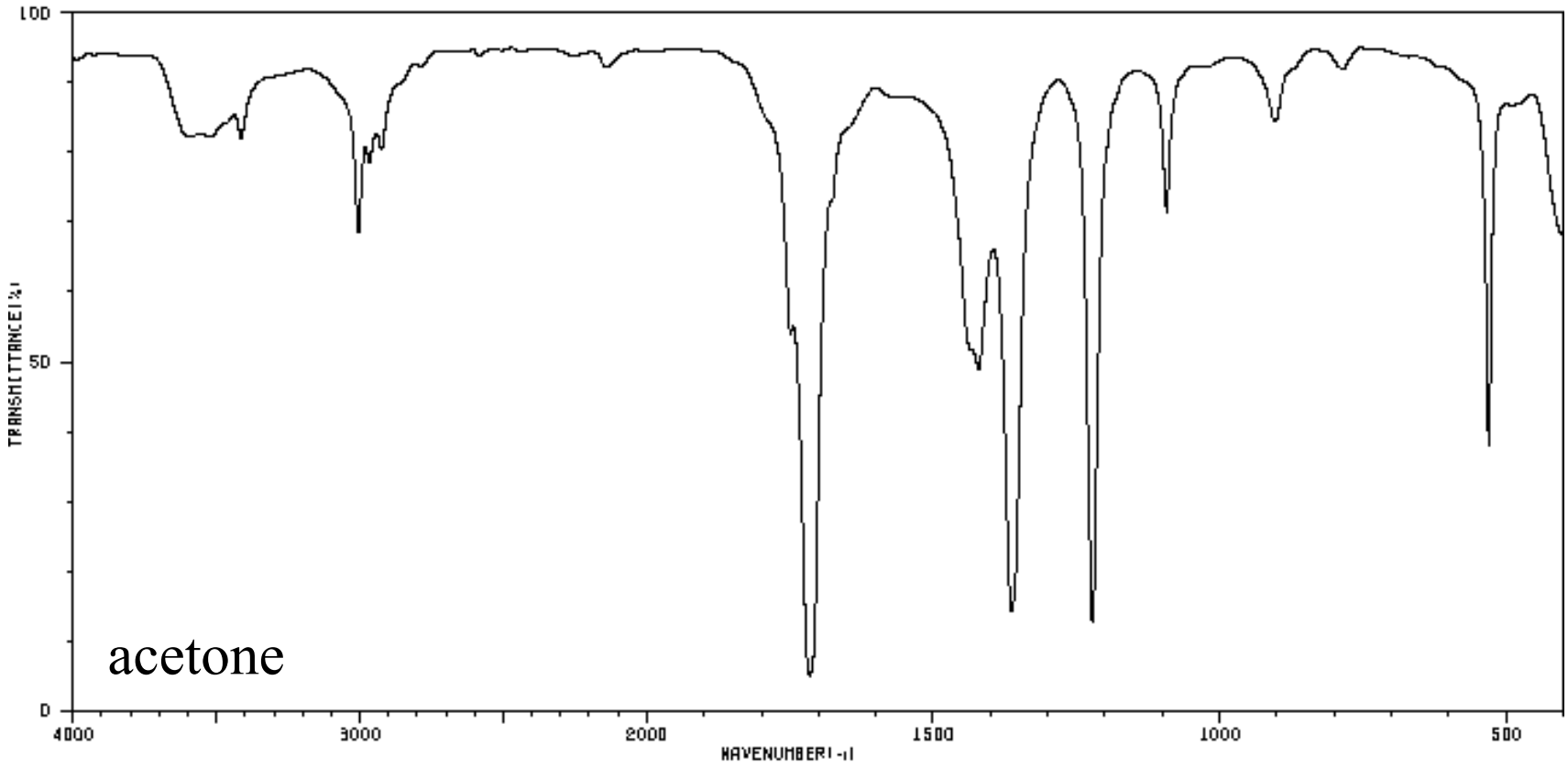
TRANSMITTANCE[%]
4000
3000
2000
1500
1000
500
WAVENUMBER[-1]
methanol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1000
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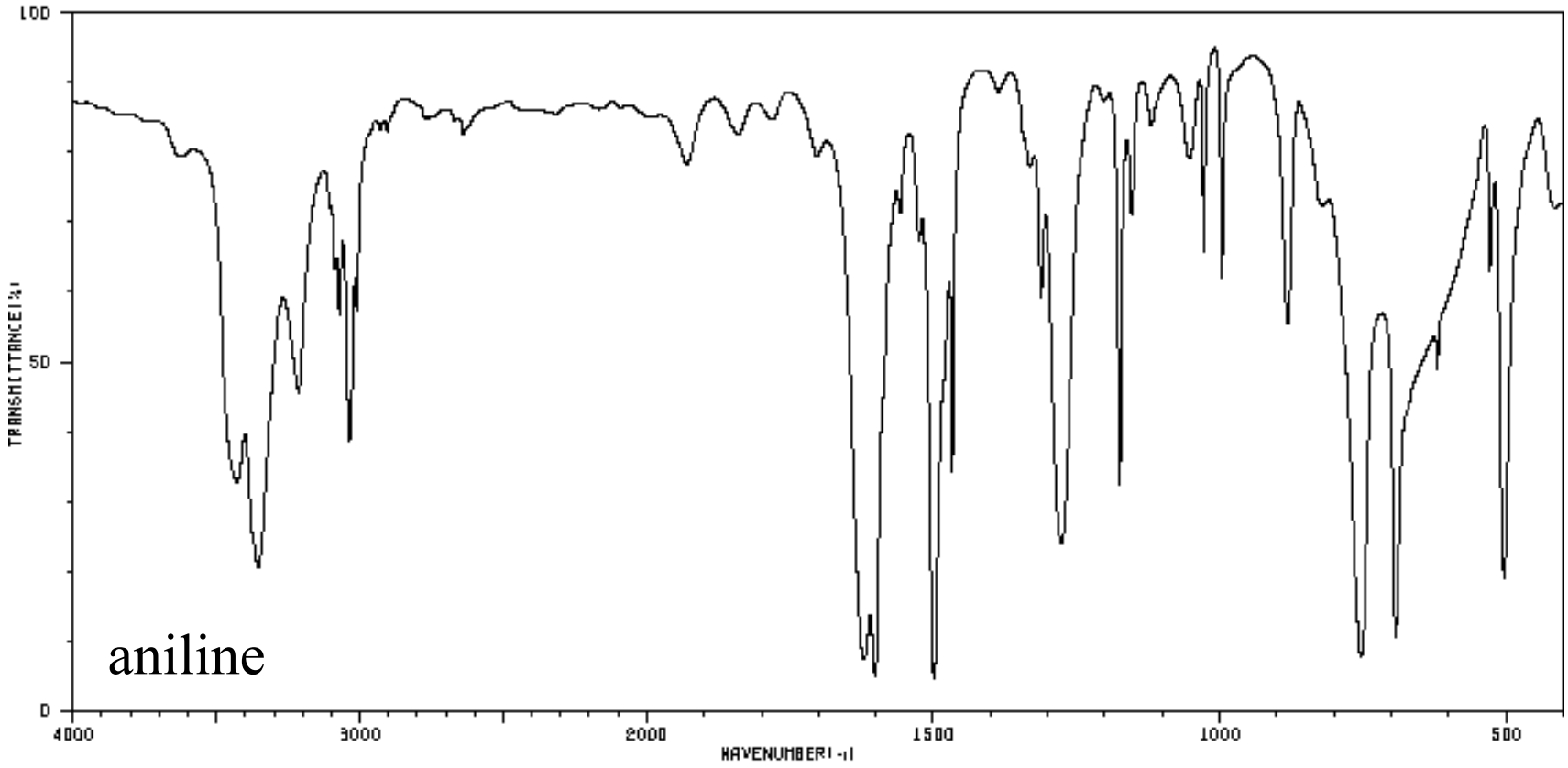
WAVENUMBER[-1]
acetone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0
TRANSMITTANCE[%]
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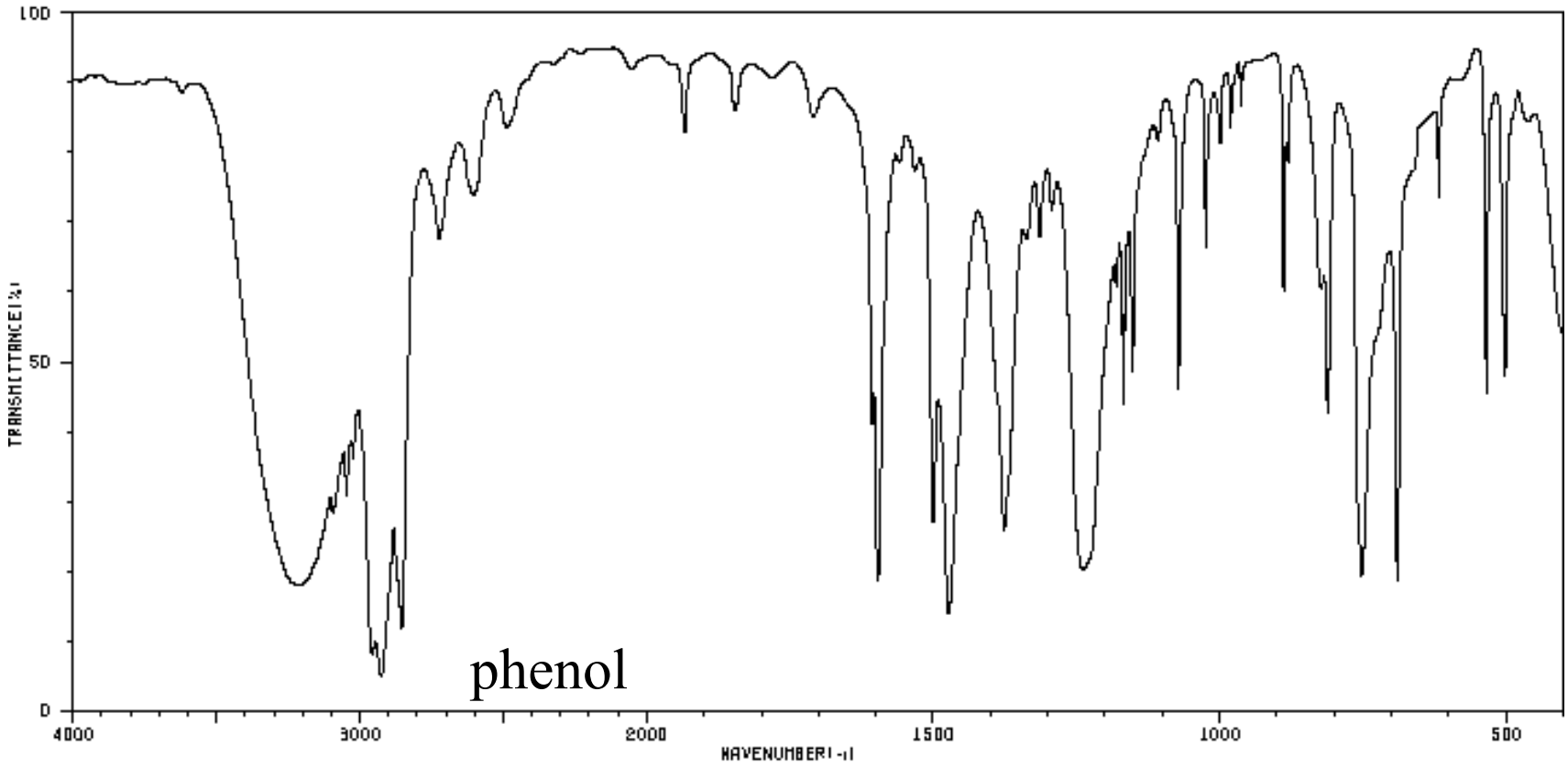
2000
1500
1000
500
WAVENUMBER[-1]
aniline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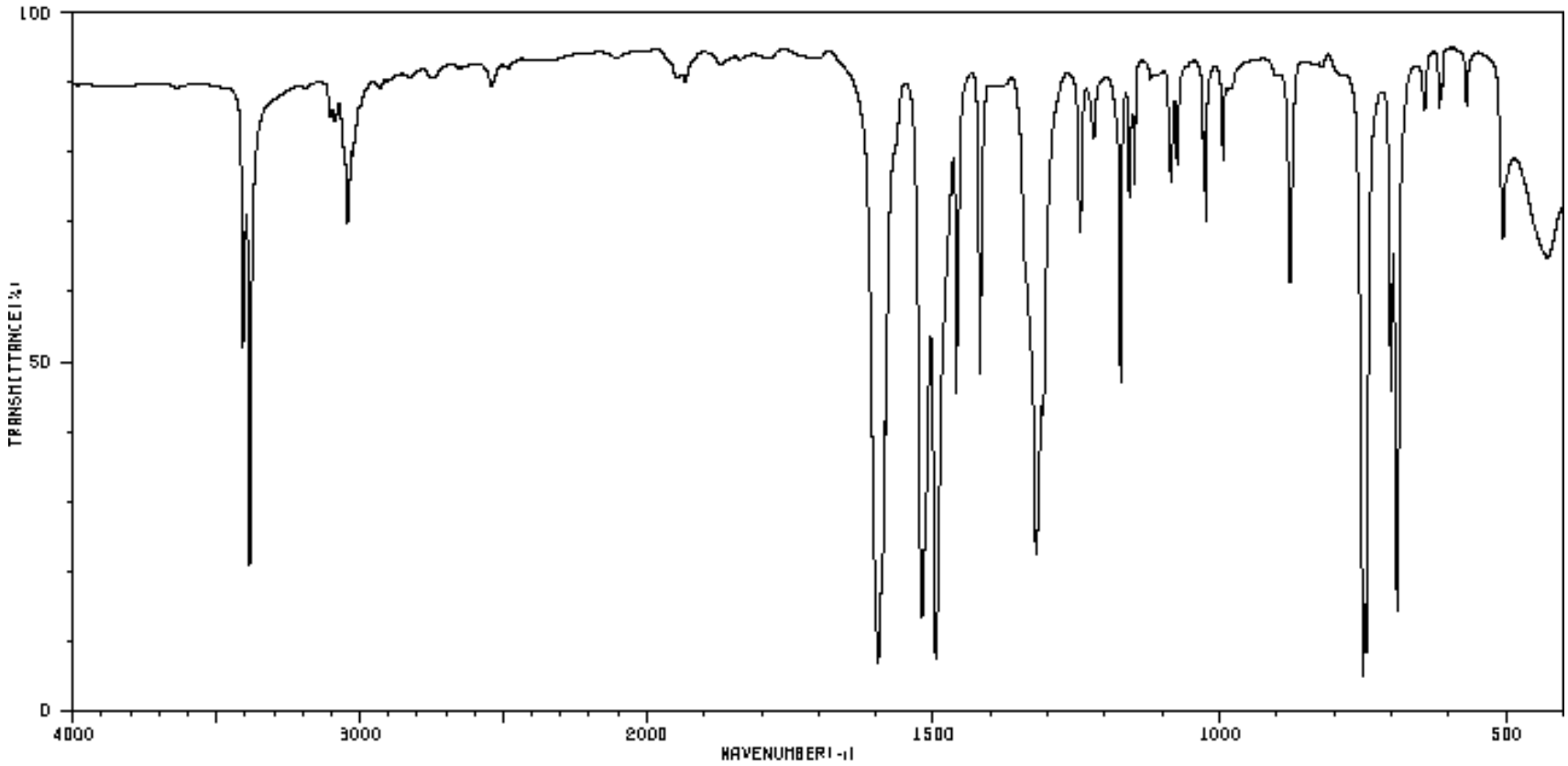
3000
2000
1500
1000
500
WAVENUMBER[-1]
phenol

HIT-NO=1941	SCORE= ( )	SDBS-NO=2350	IR-NIDA-07683 : KBR DISC

DIPHENYLAMINE

$C_{12}H_{11}N$



3408	60	1596	6	1308	41	1086	72	746	7
3384	20	1583	37	1244	66	1074	74	702	43
3102	81	1520	12	1220	79	1029	79	690	13
3087	81	1496	7	1180	79	1024	68	643	84
3052	74	1460	43	1173	44	994	77	506	64
3042	68	1419	45	1156	70	877	58	499	74
3026	77	1321	21	1149	72	760	4	429	62