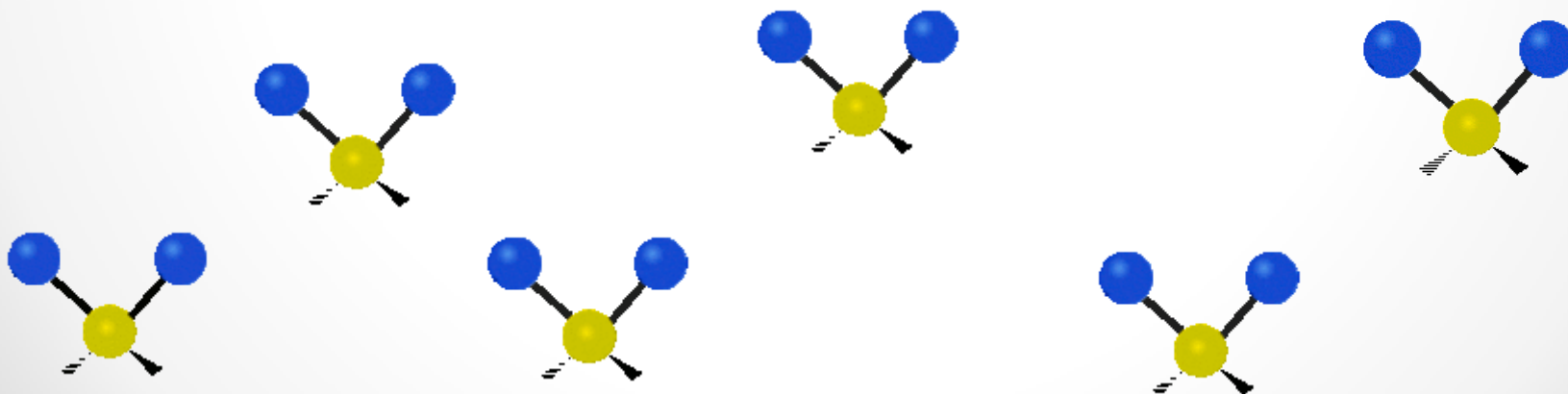


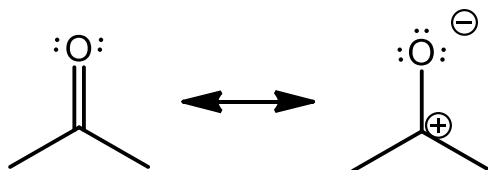
IR – Spectroscopy

Part II



Carbonyl - compounds

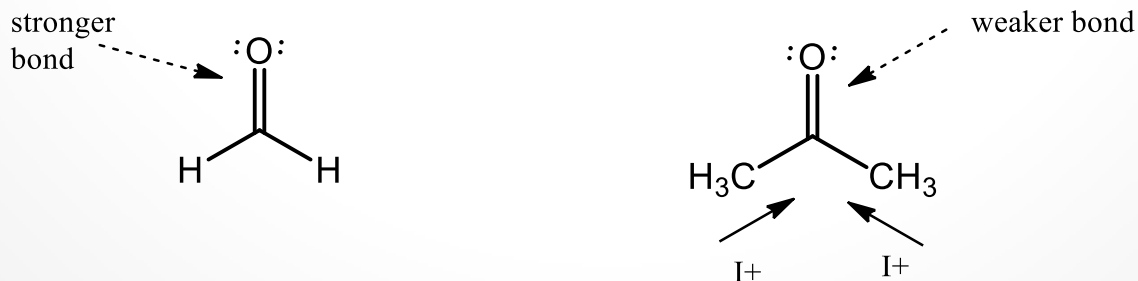
For simple aldehydes and ketones, the stretching vibration of the carbonyl group has a strong infrared absorption between 1710 and 1740 cm^{-1} .



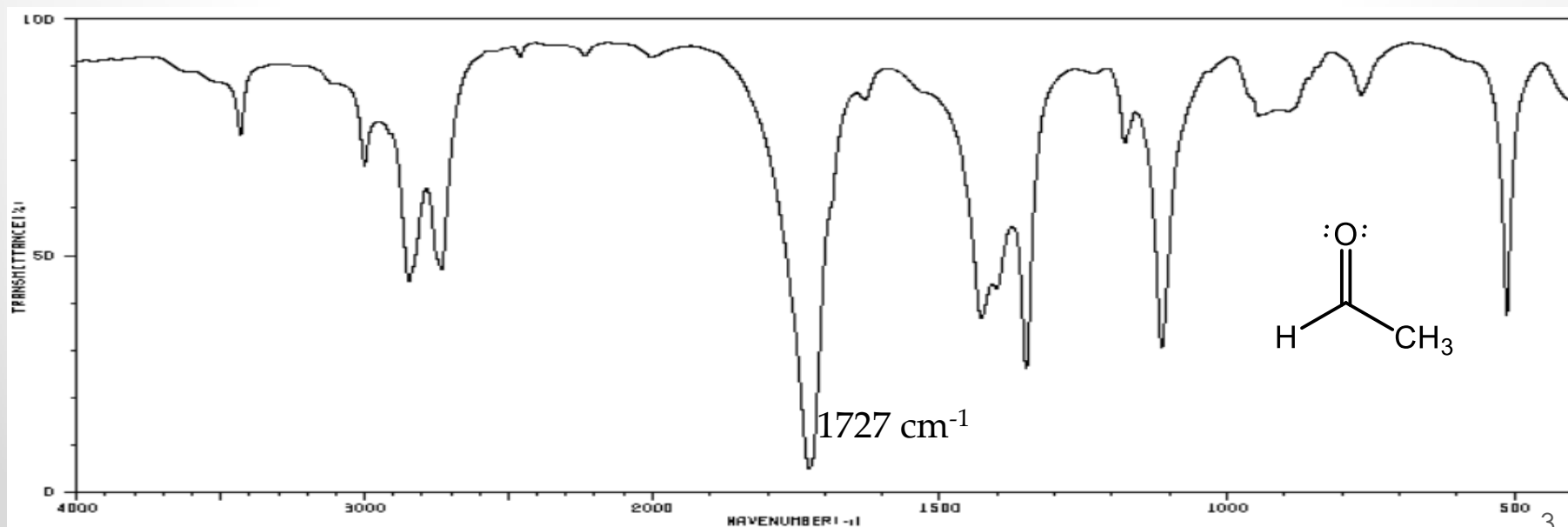
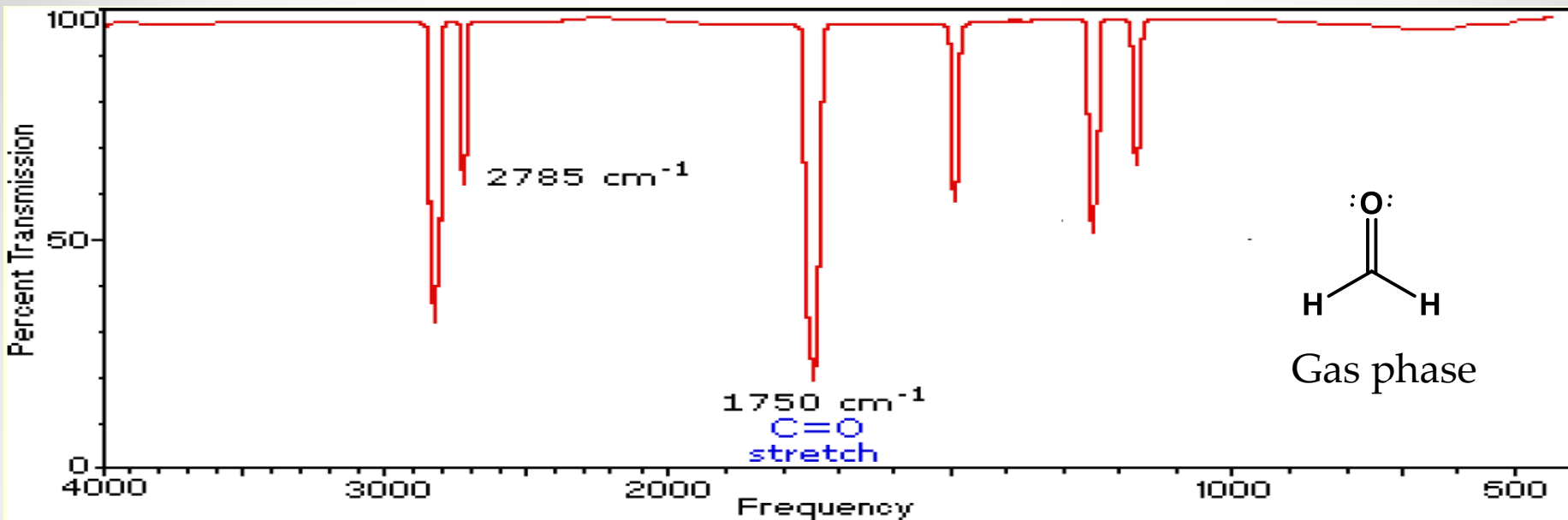
Alkyl substituents are **Electron Donating Groups**

– inductive effect lower the bond strength of $\text{C}=\text{O}$

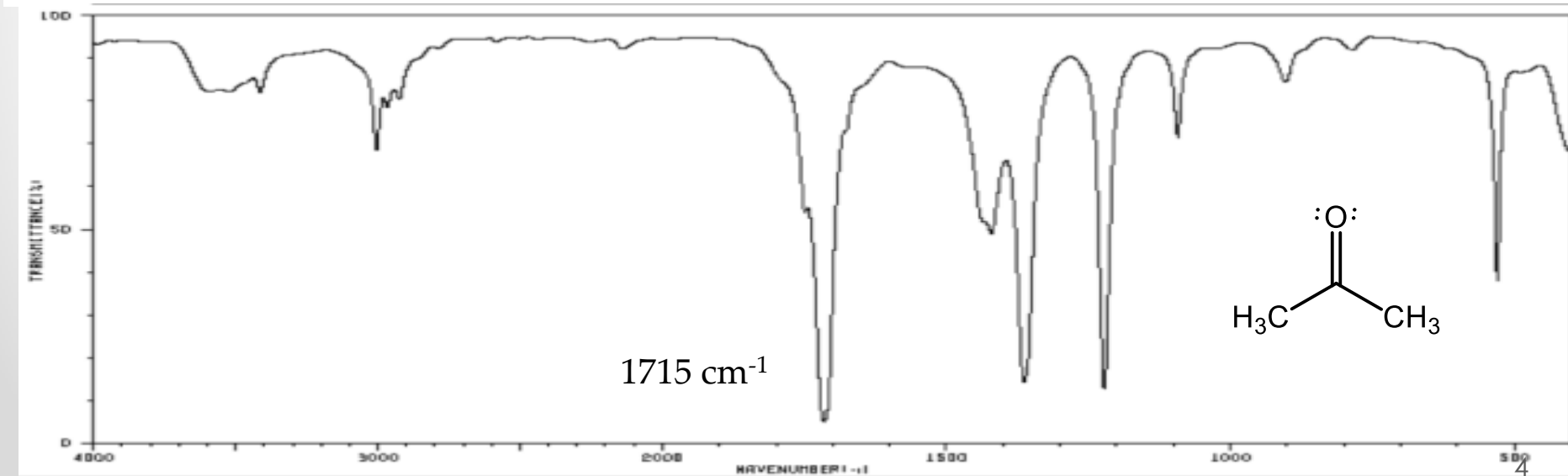
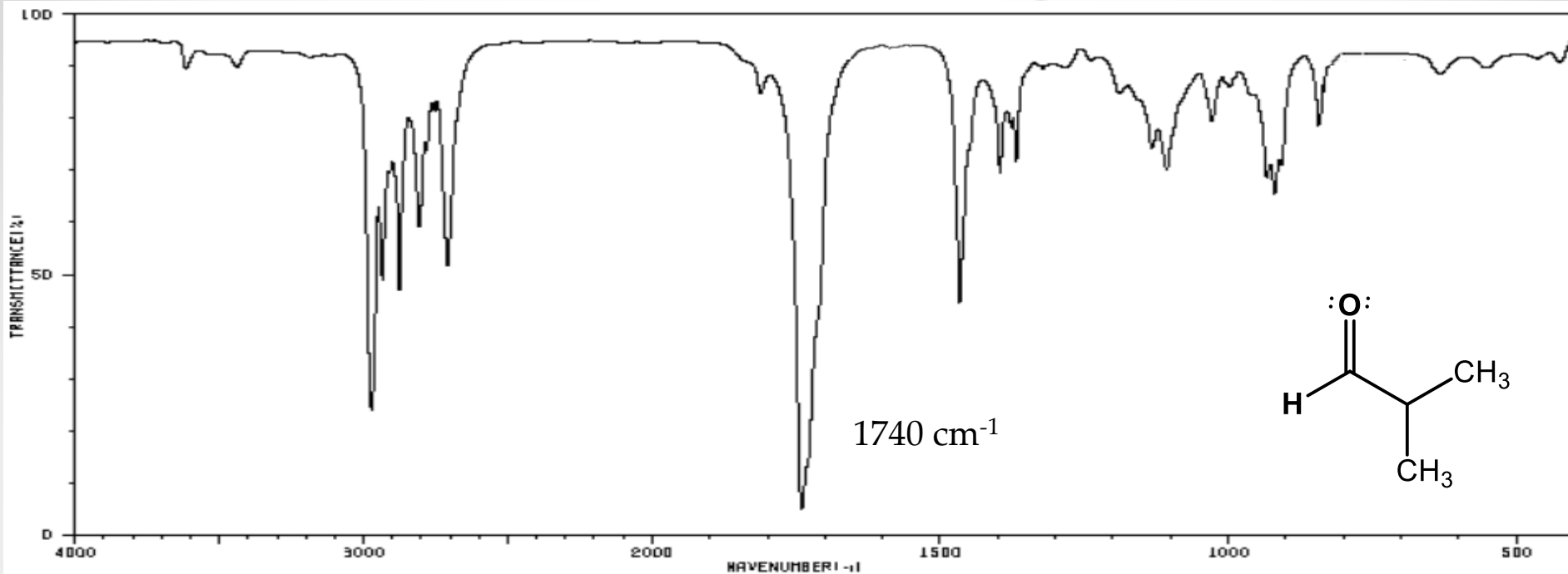
ketone carbonyls have slightly lower stretching frequencies, $1715 \pm 7\text{ cm}^{-1}$, compared with aldehydes, $1730 \pm 7\text{ cm}^{-1}$.



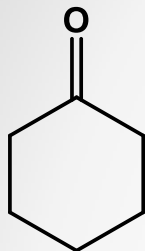
Ketones and aldehydes



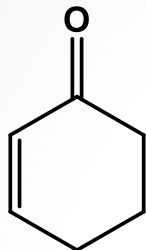
Ketones and aldehydes



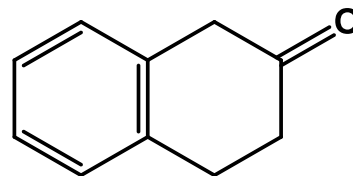
Ketones and aldehydes – conjugated systems



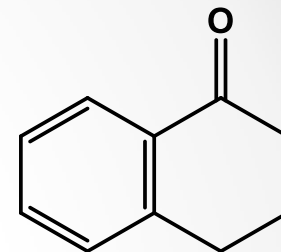
1716 cm^{-1}



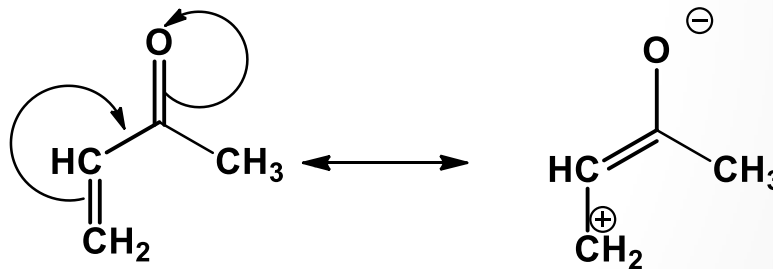
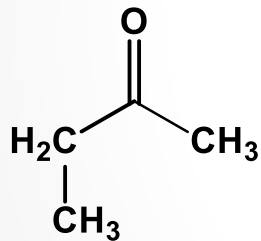
1685 cm^{-1}
(C=C) 1617 cm^{-1}



1716 cm^{-1}



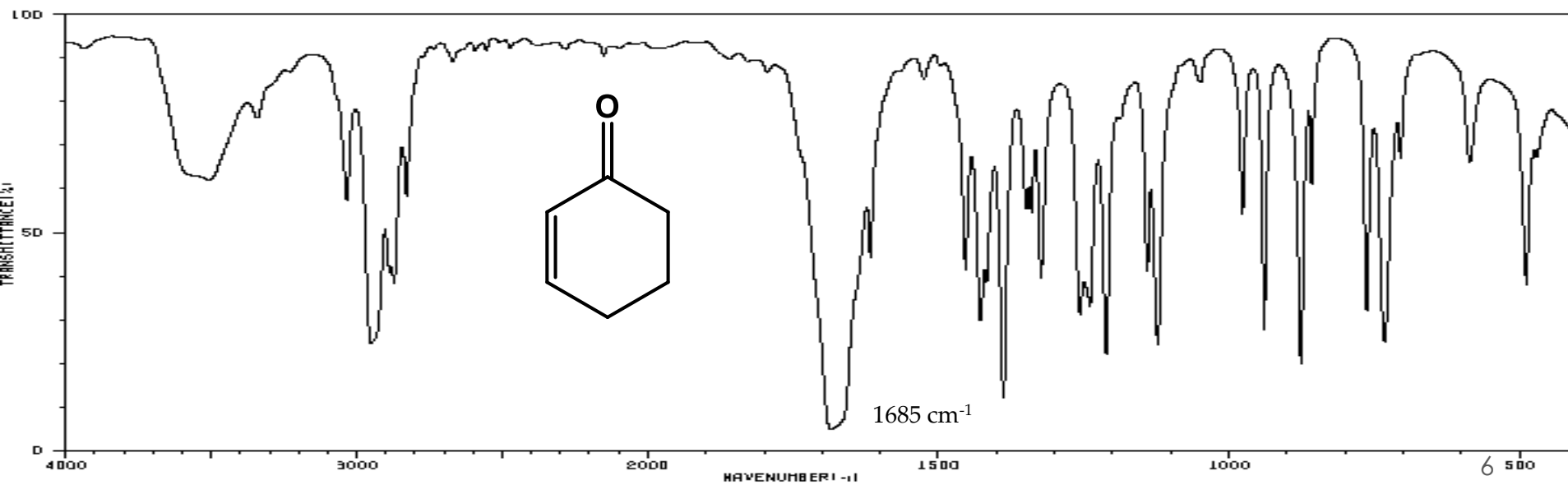
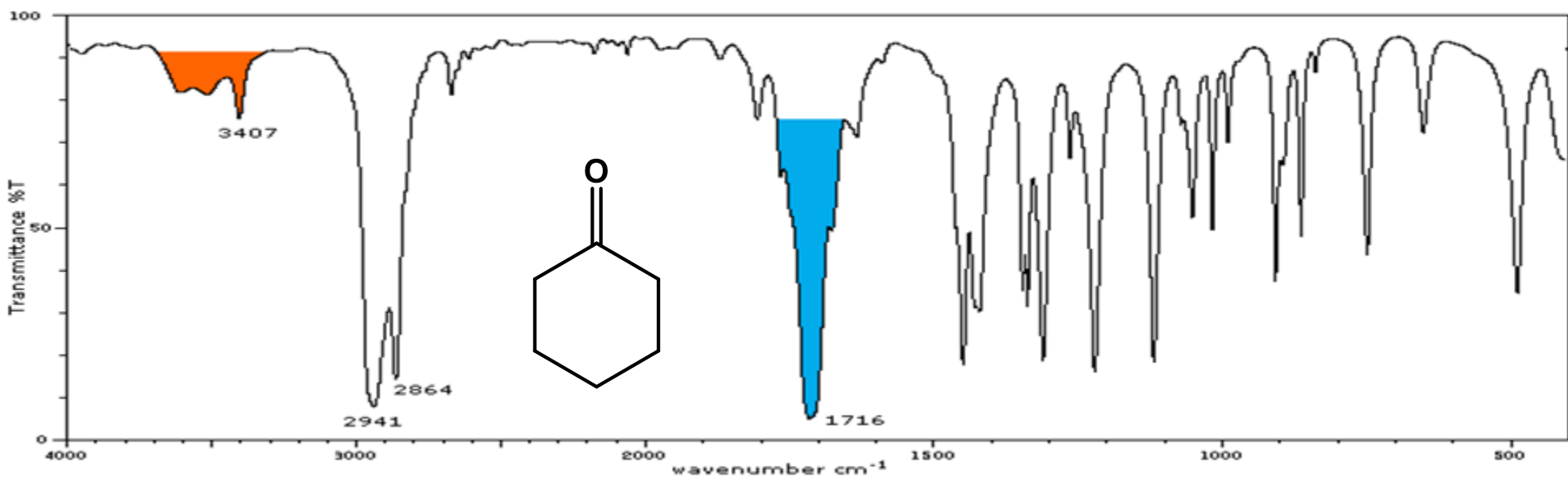
1683 cm^{-1}



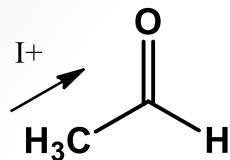
weaker carbonyl bond

Conjugation of C=O bond with a double bond or phenyl ring lowers the stretching frequency.

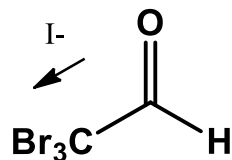
Ketones and aldehydes – conjugated systems



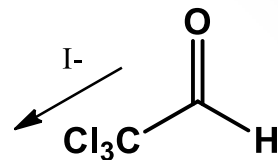
Ketones and aldehydes – influence of EDG and EWG



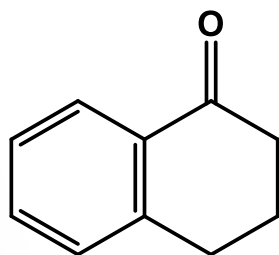
1727 cm^{-1}



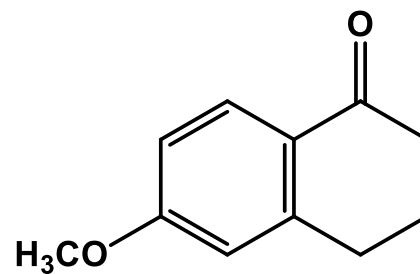
1741 cm^{-1}



1768 cm^{-1}

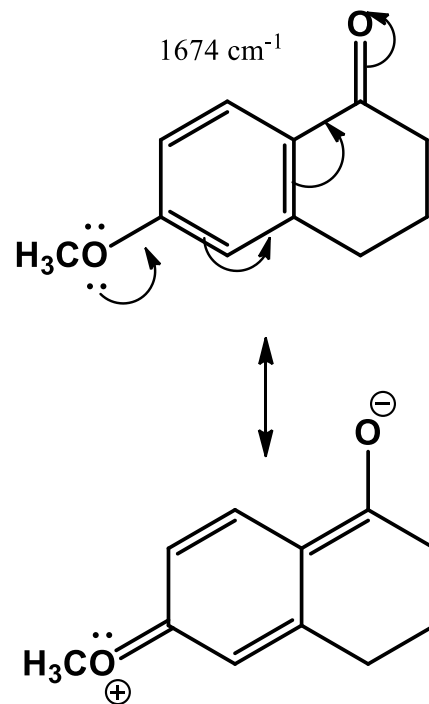
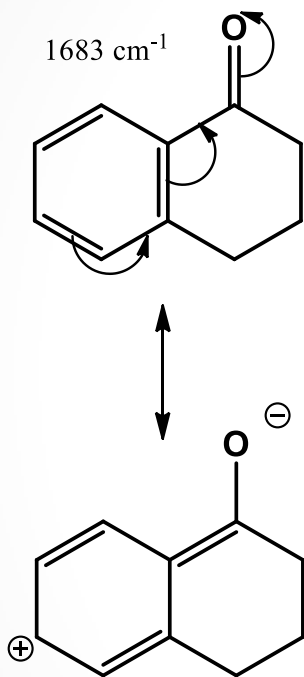


1683 cm^{-1}



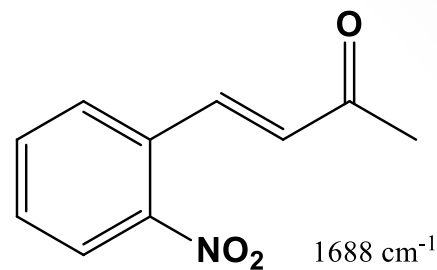
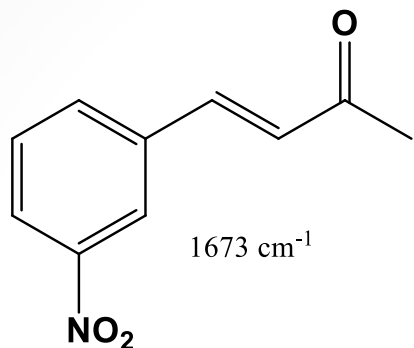
1674 cm^{-1}

Ketones and aldehydes – influence of EDG and EWG



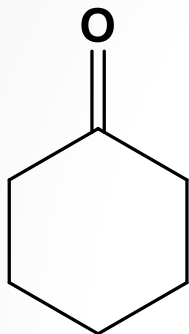
all atoms with electron octet

Ketones and aldehydes – influence of EDG and EWG

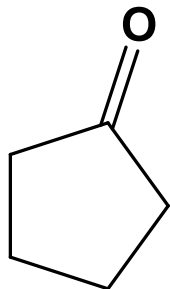


Two above isomeric ketones has different absorbtion of $\text{C}=\text{O}$ group,
Please, draw appropriate mesomeric structures to explain observed facts.

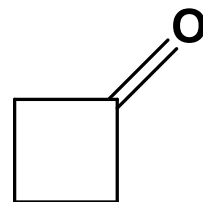
Ketones– ring size



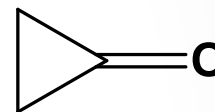
1715 cm^{-1}



1748 cm^{-1}



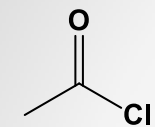
1785 cm^{-1}



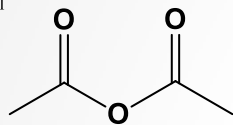
1850 cm^{-1}

Incorporation of the carbonyl group into a small ring, increase the stretching frequency.

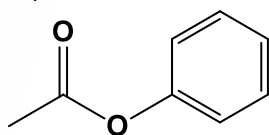
Carbonyl compounds



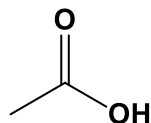
1807 cm^{-1}



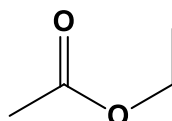
1761 cm^{-1}
1832 cm^{-1}



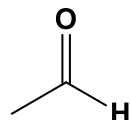
1768 cm^{-1}



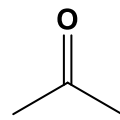
1760 cm^{-1}
monomer



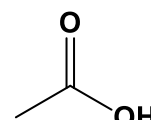
1749 cm^{-1}



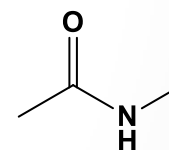
1731 cm^{-1}



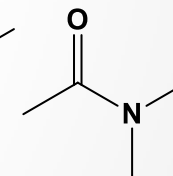
1719 cm^{-1}



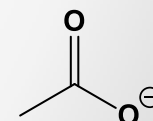
1710 cm^{-1}
dimer



1688 cm^{-1}

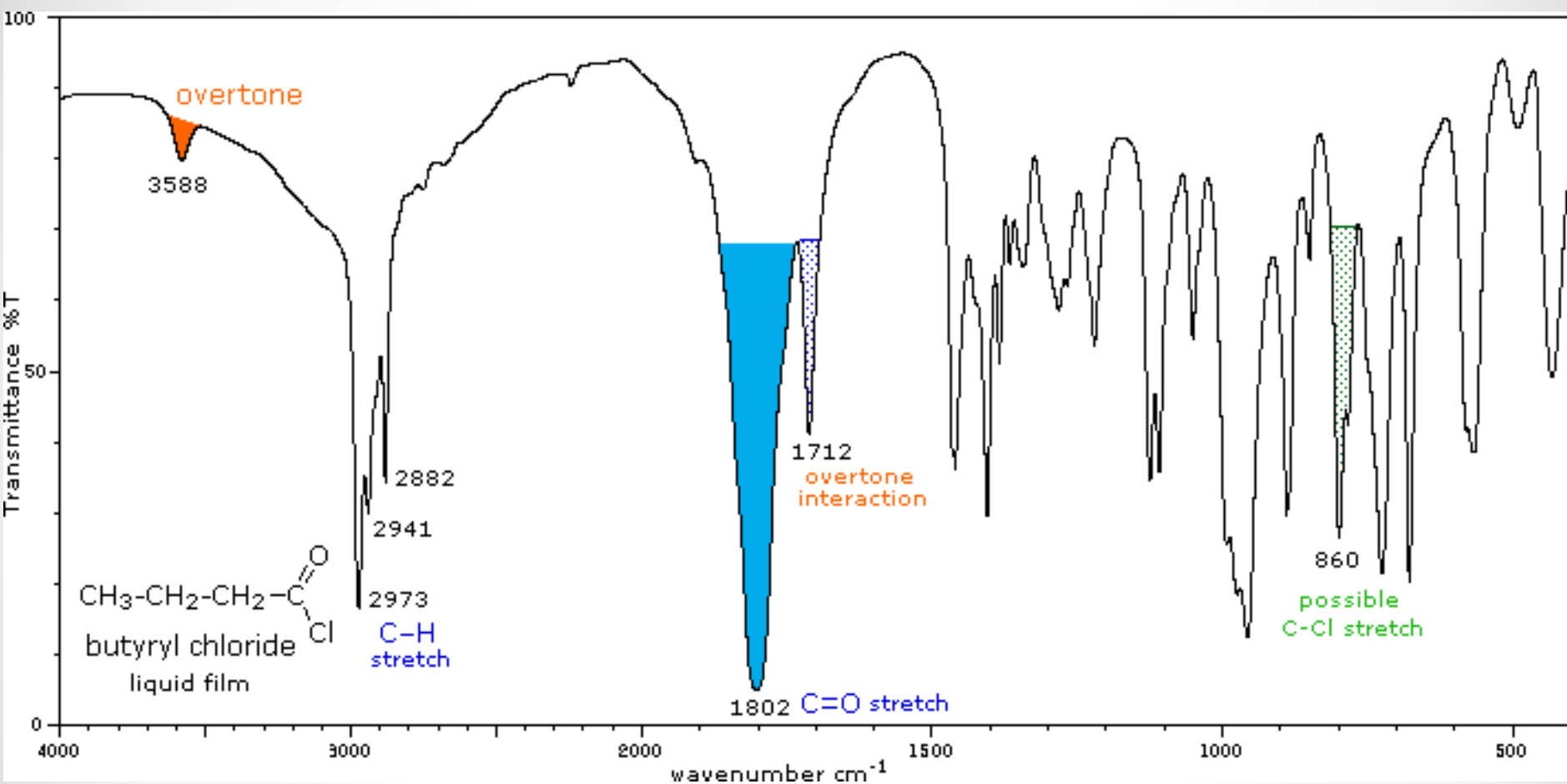


1662 cm^{-1}



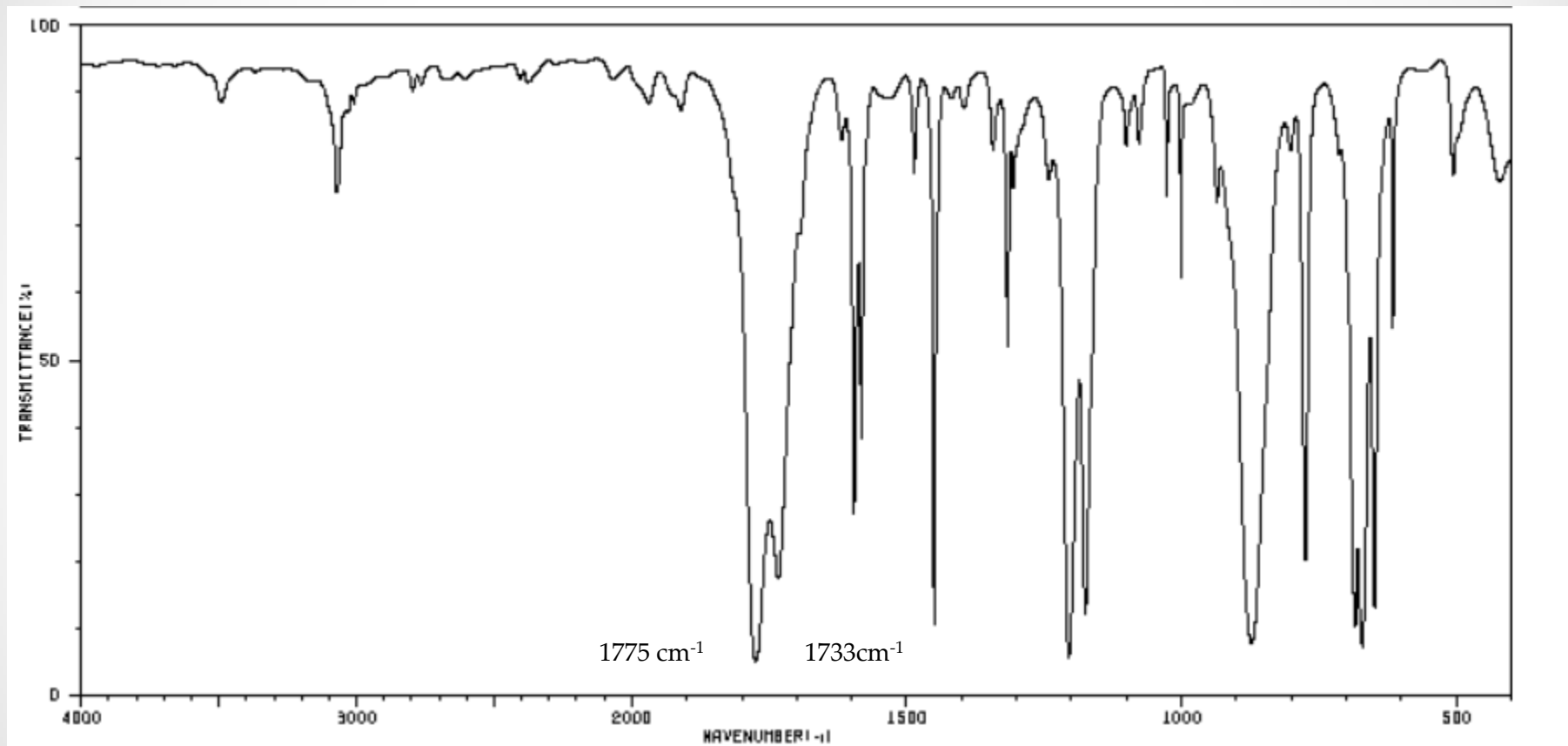
1413 cm^{-1}
1563 cm^{-1}

Acid chlorides –aliphatic - butyryl chloride

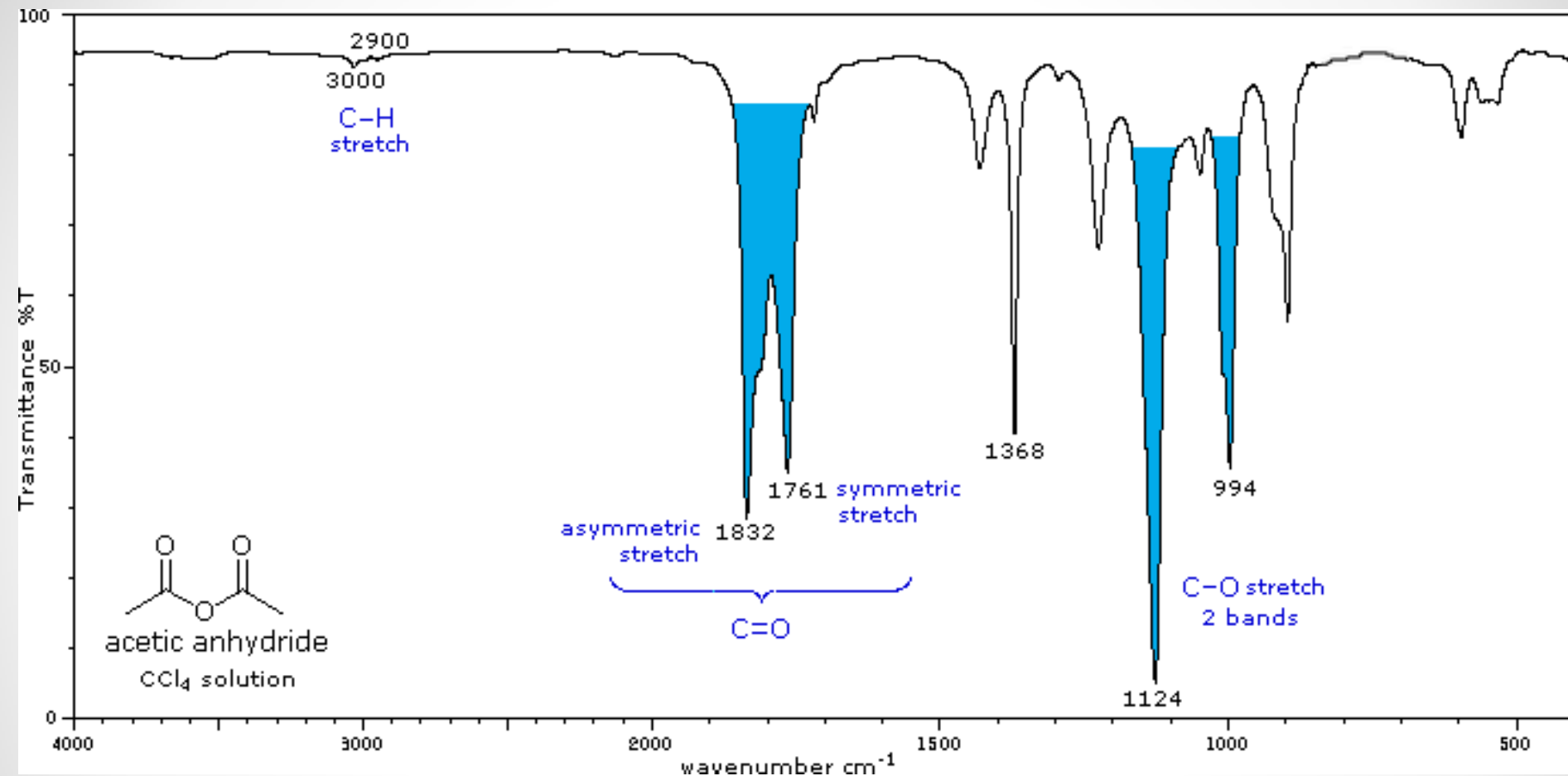


Additional band in C=O region is a result of Fermi resonance of C-Cl and C=O

Acid chlorides –aromatic - benzoyl chloride



Carboxylic anhydrides



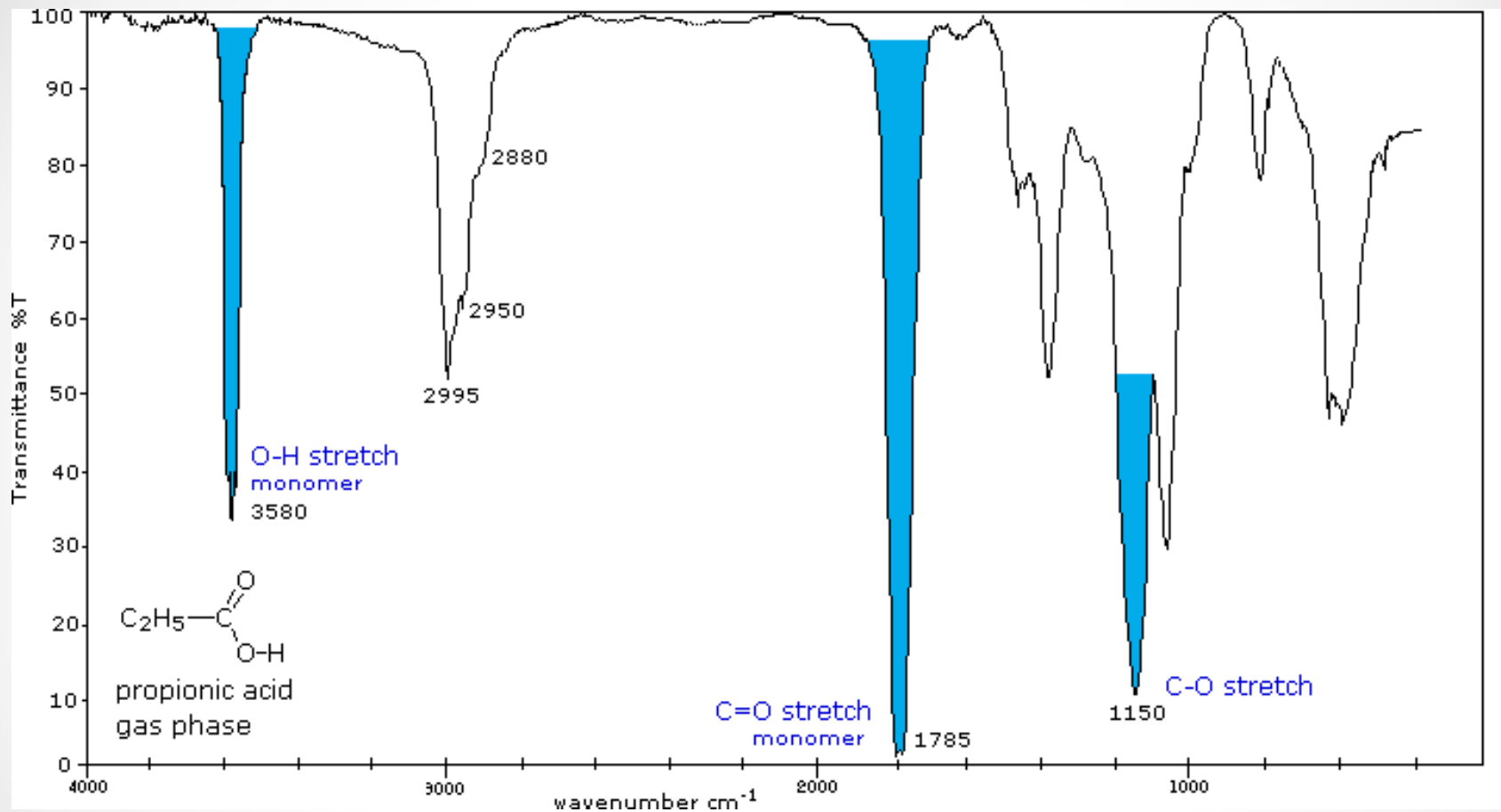
Anhydrides C=O stretch: 2 bands separated by 60 -30 cm⁻¹)

Acyclic anhydrides, 1750 and 1820 cm⁻¹;

6-membered ring, 1750 and 1820;

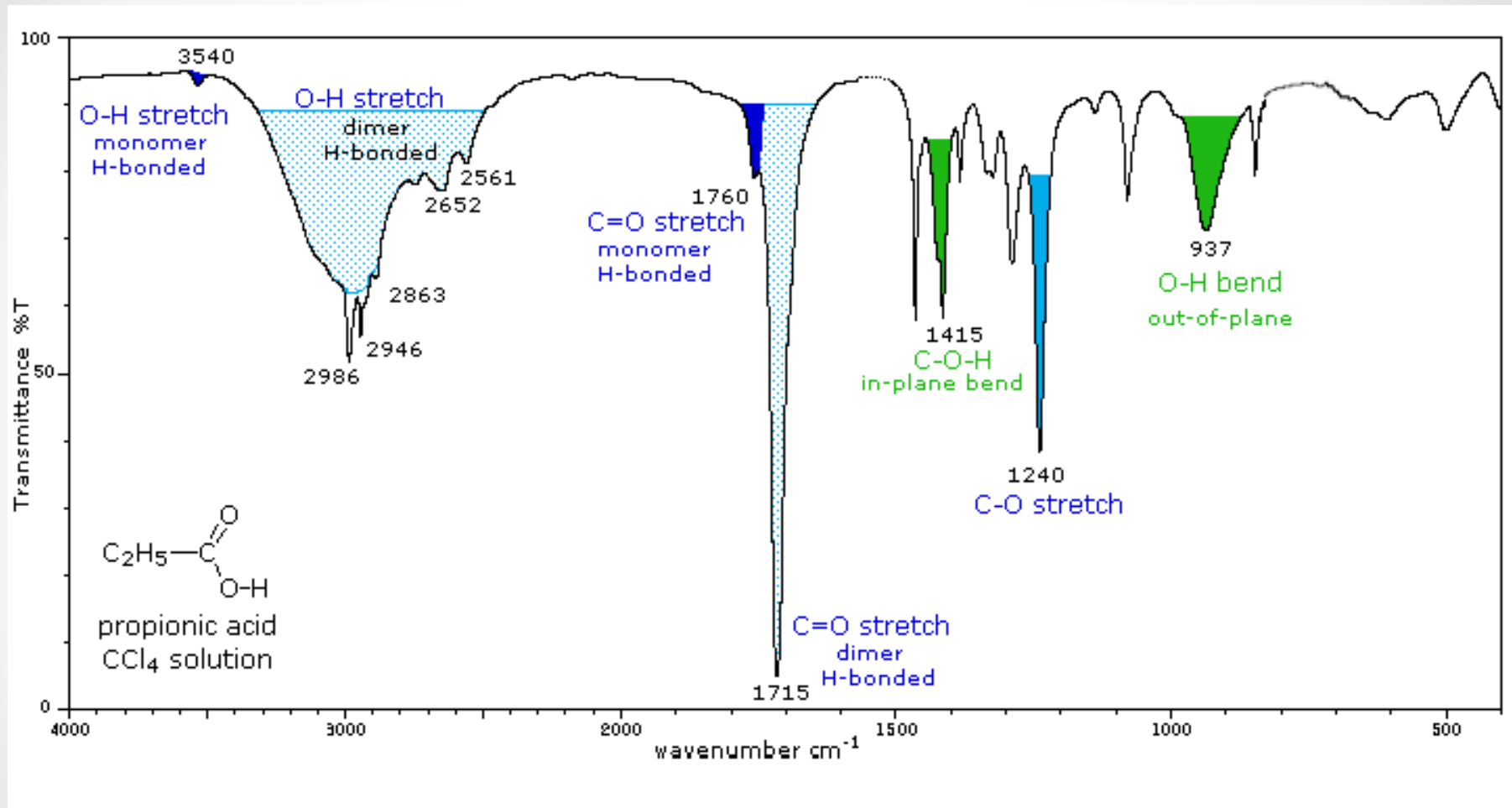
5-membered ring, 1785 and 1865

Carboxylic acid – hydrogen bonds



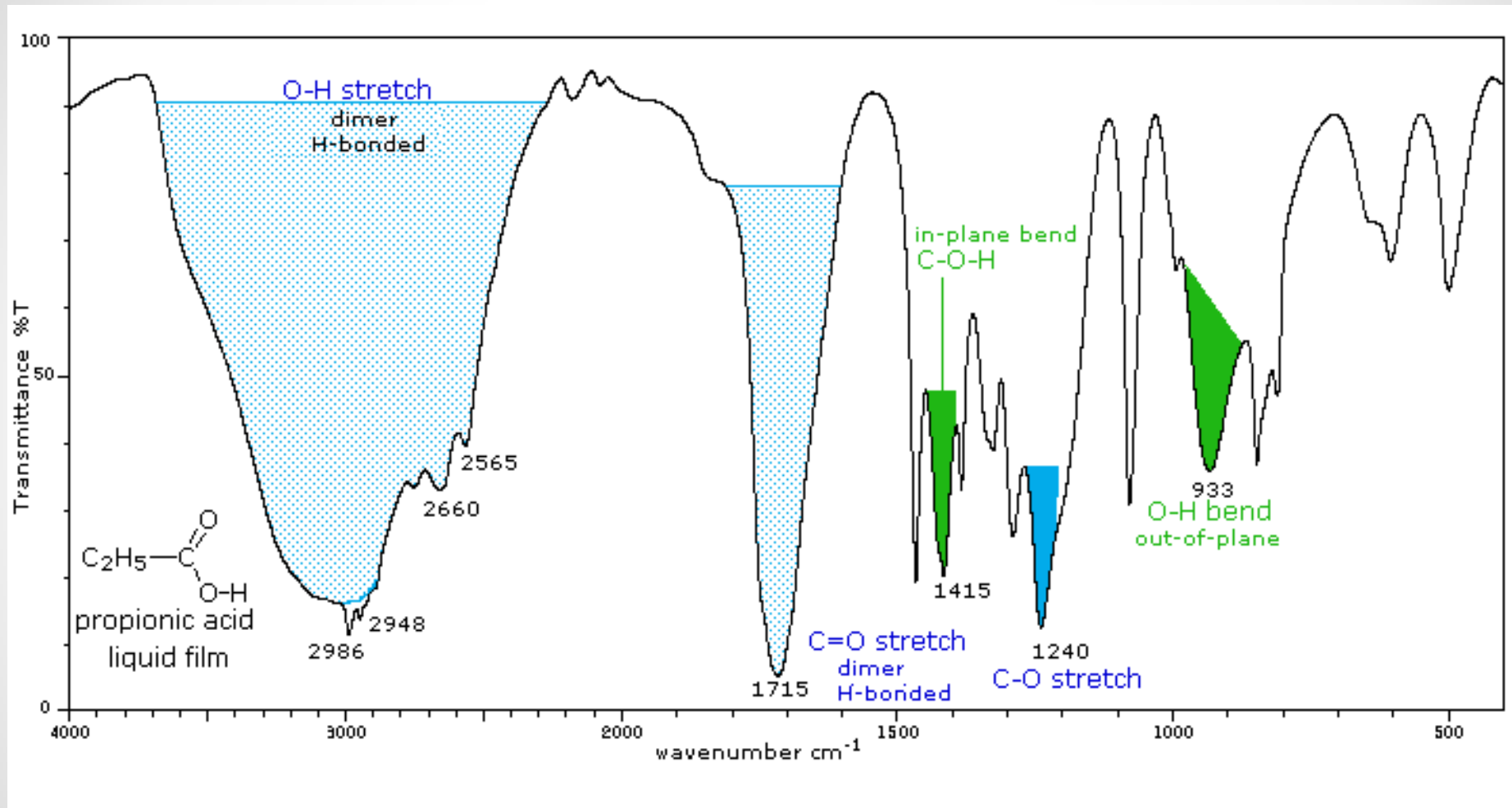
Spectrum of carboxylic acid in gas phase – only monomeric molecules

Carboxylic acid – hydrogen bonds



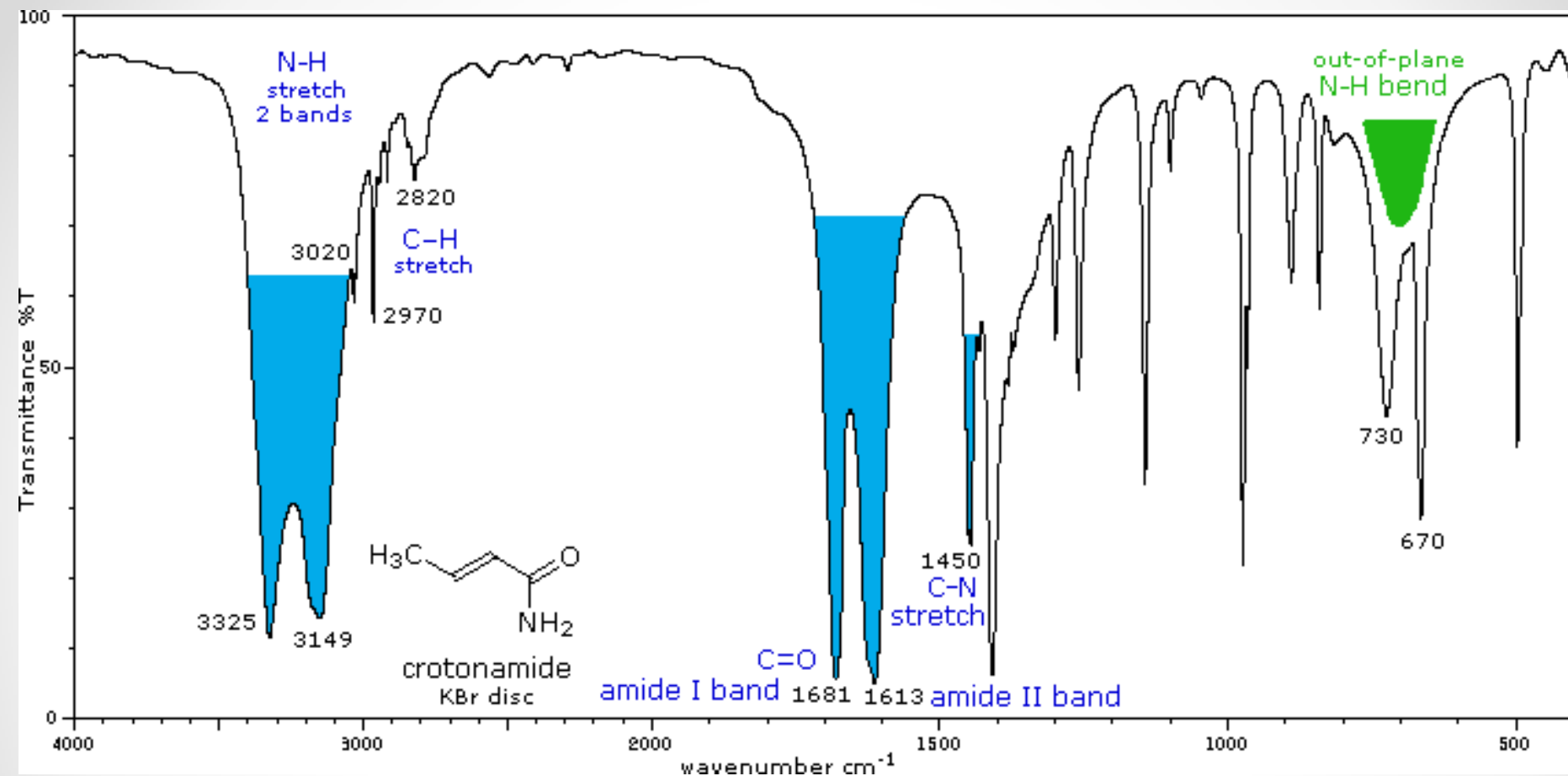
Spectrum of carboxylic acid in solution– dimeric and monomeric

Carboxylic acid – hydrogen bonds



Spectrum of liquid carboxylic acid (pure substance) – only dimer is observed

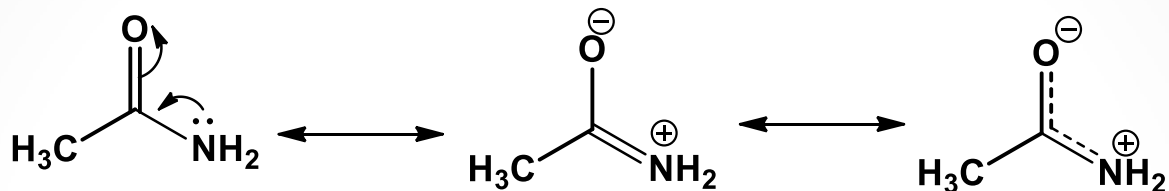
Primary Amides



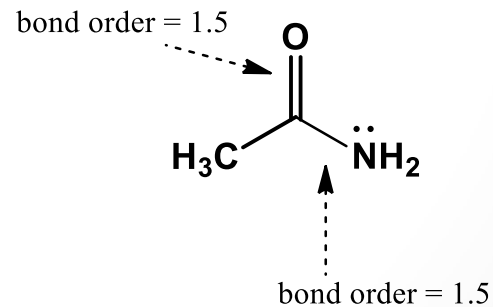
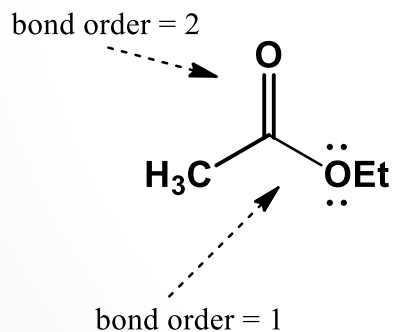
Amide I band ν C=O stretching, Amide II band δ N-H bending in plane

Why the wavenumber of I amide band is usually below 1700 cm^{-1} ?

Amides bond properties

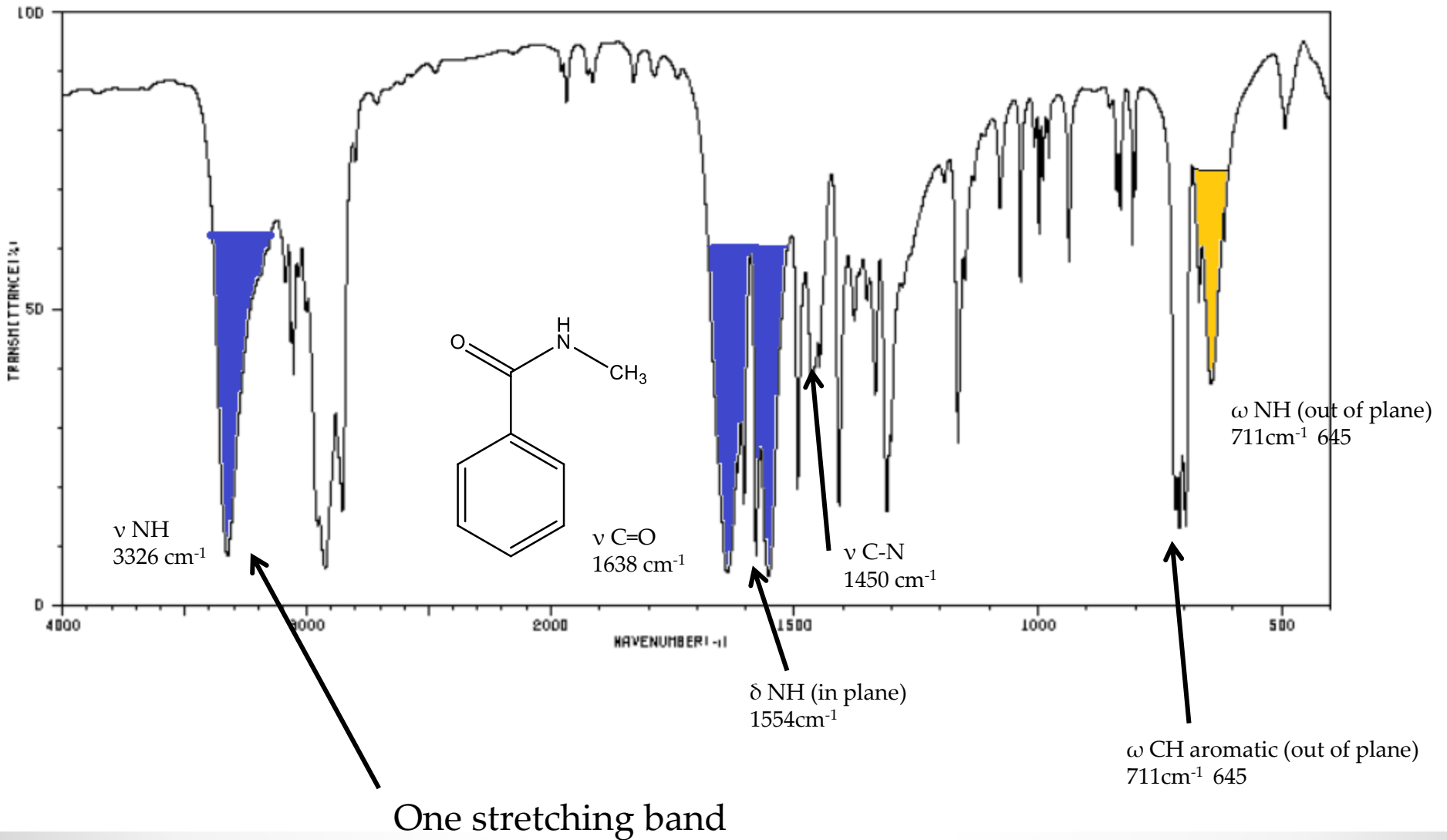


$-\text{NH}_2$ is strong EDG, lone electron pair on nitrogen is conjugated with C=O bond

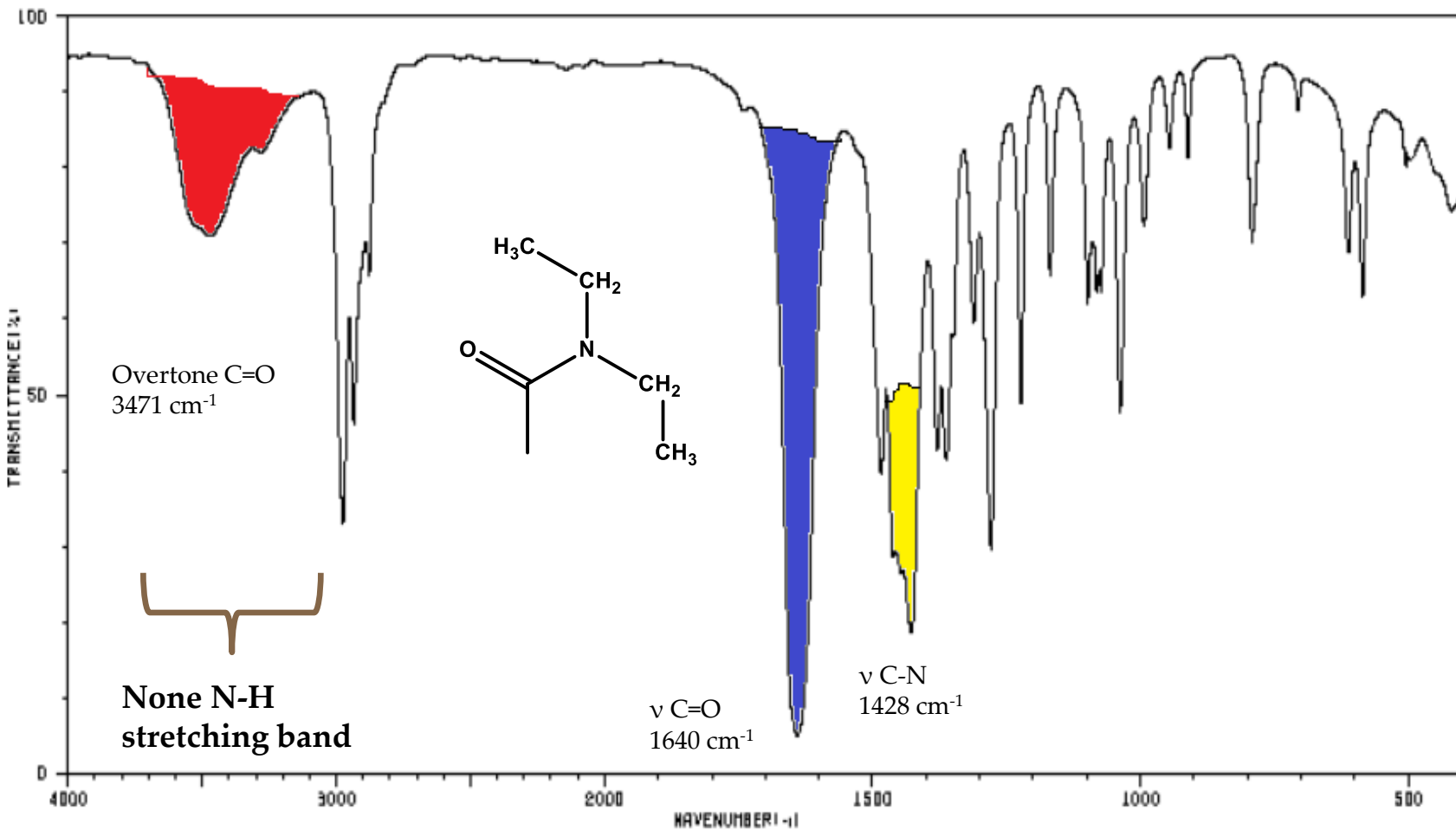


Conjugation of C=O bond with an EDG : (lone pair, double bond or phenyl ring) lowers the stretching frequency.

Secondary Amides



Tertiary Amides

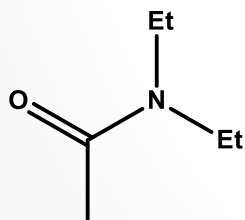


Lactams

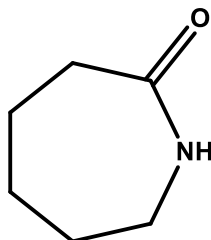
- 1° & 2°-amides, 1510 to 1700 cm^{-1} (2 bands)
- 3°-amides, 1650 ± 15 (one band);
- 6-membered lactams, 1670 ± 10 (one band)
- 5-membered lactams, 1700 ± 15 ;
- 4-membered lactams, 1745 ± 15 .

} non-cyclic amides

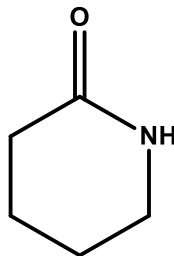
} cyclic amides



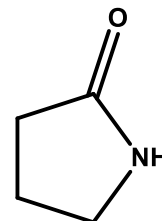
$\nu \text{ C=O}$
 1640 cm^{-1}



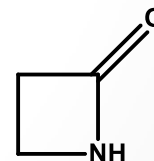
$\nu \text{ C=O}$
 1671 cm^{-1}



$\nu \text{ C=O}$
 1666 cm^{-1}



$\nu \text{ C=O}$
 1700 cm^{-1}



$\nu \text{ C=O}$
 1745 cm^{-1}

Lactones

Esters, $1740 \pm 10 \text{ cm}^{-1}$;



non-cyclic esters

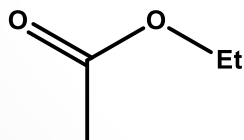
6 membered lactone, $1740 \pm 10 \text{ cm}^{-1}$;

5 membered lactone, $1765 \pm 10 \text{ cm}^{-1}$;

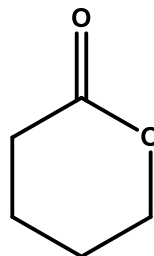
4 membered lactone, $1840 \pm 5 \text{ cm}^{-1}$



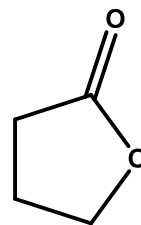
cyclic esters



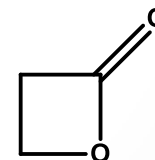
$\nu \text{ C=O}$
 1749 cm^{-1}



$\nu \text{ C=O}$
 1740 cm^{-1}

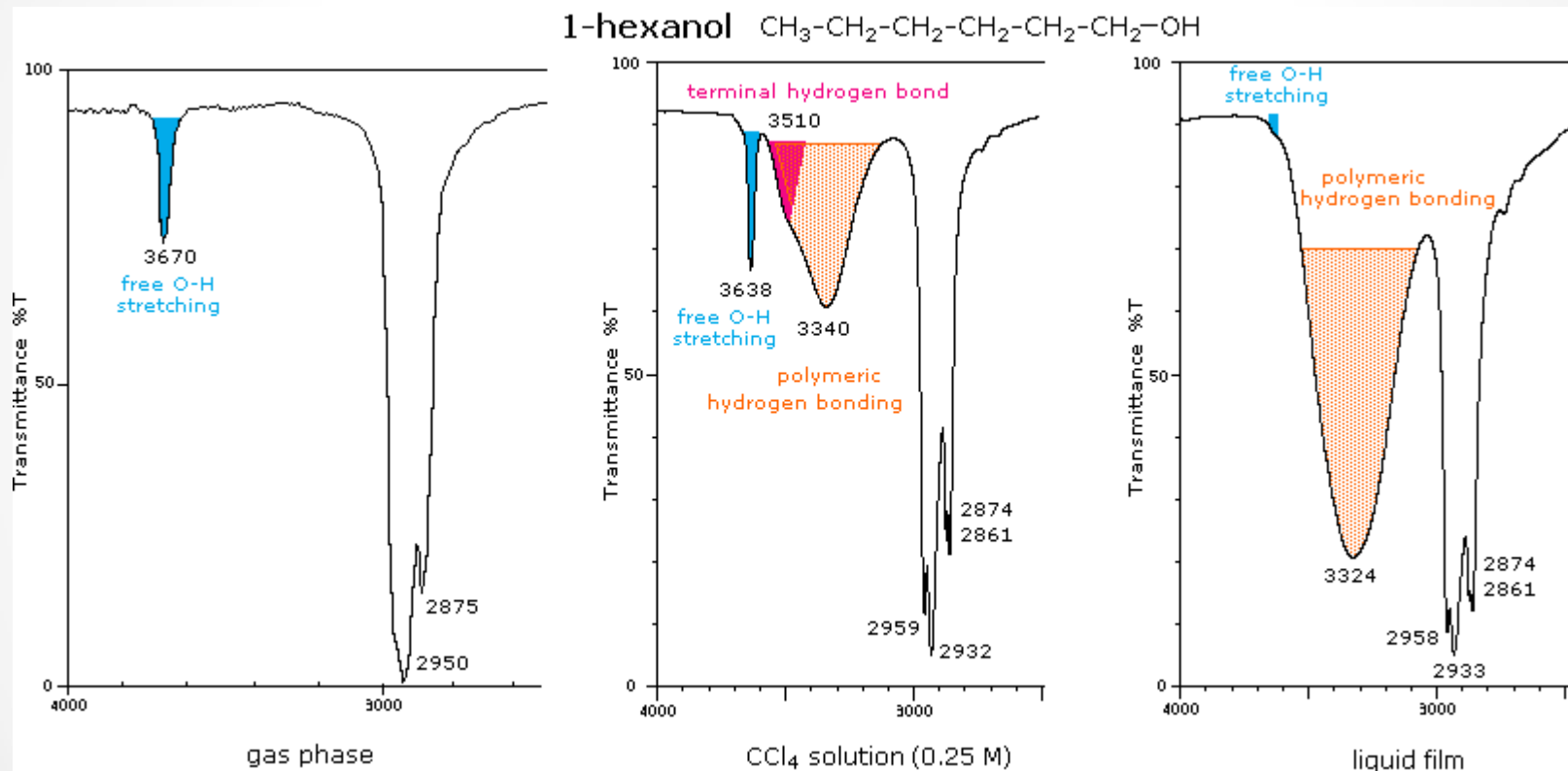


$\nu \text{ C=O}$
 1775 cm^{-1}



$\nu \text{ C=O}$
 1818 cm^{-1}

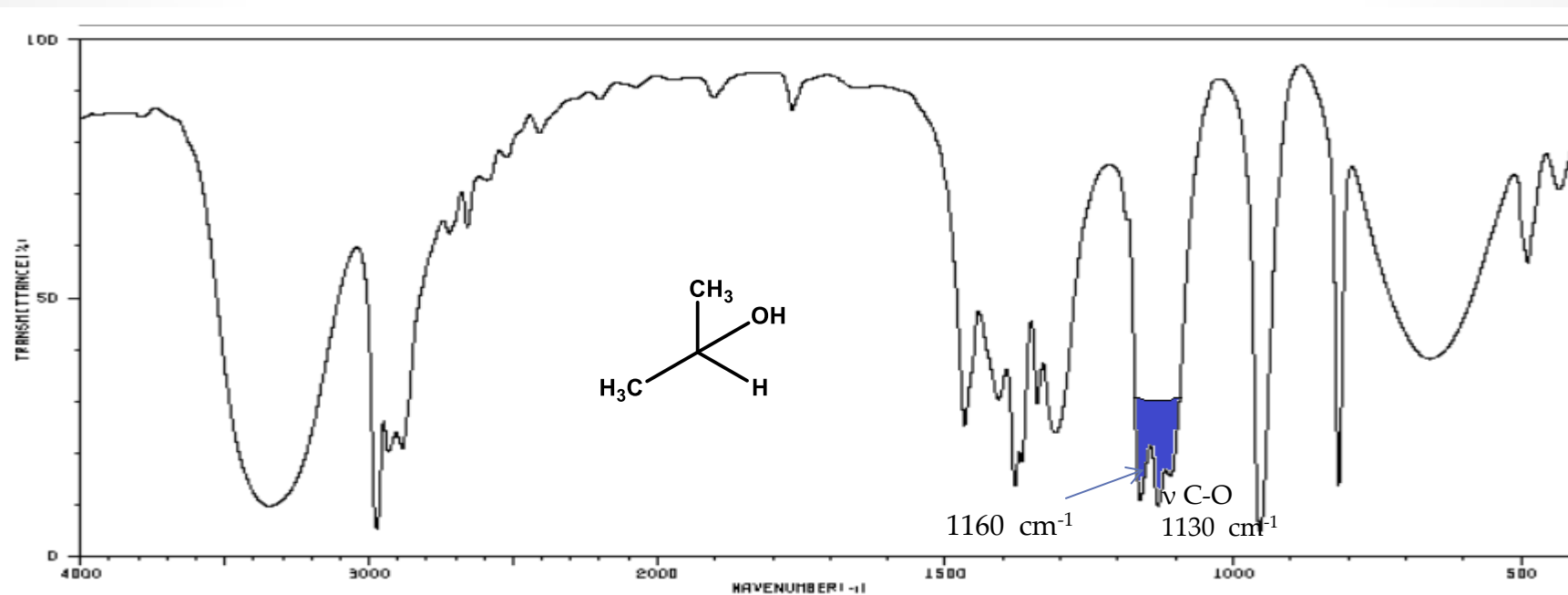
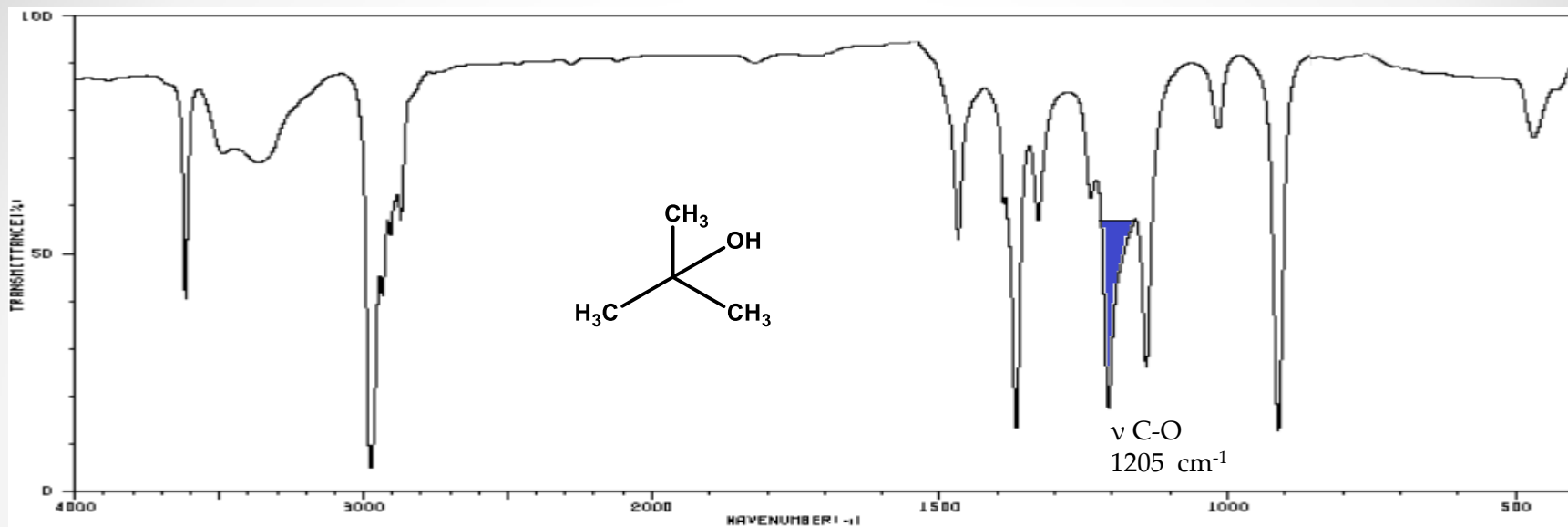
Alcohols – hydrogen bonds



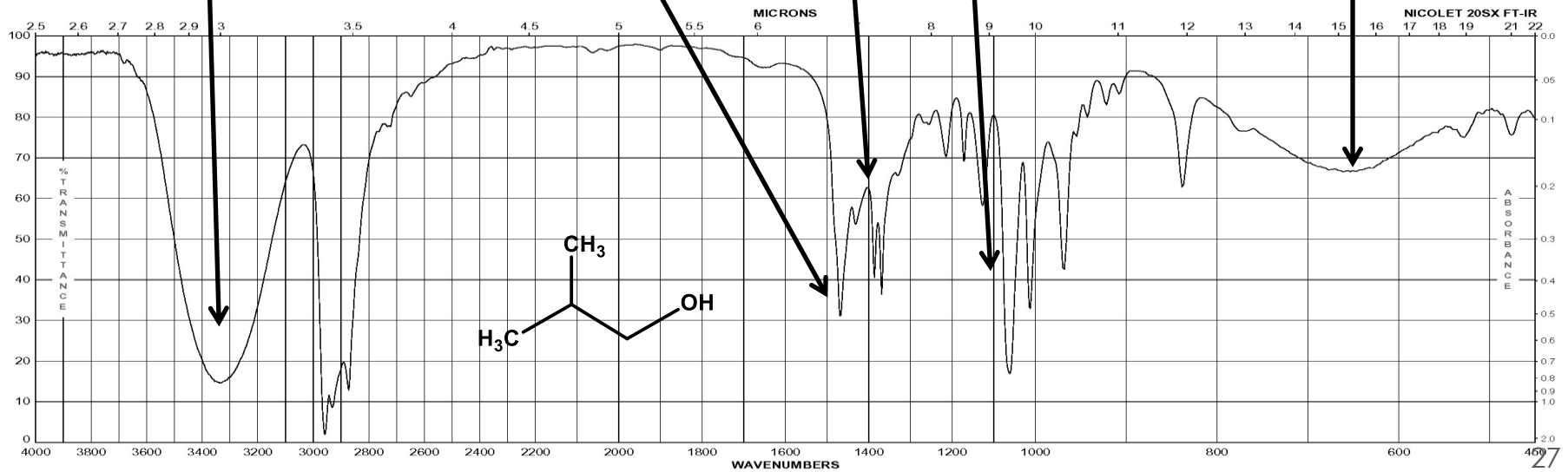
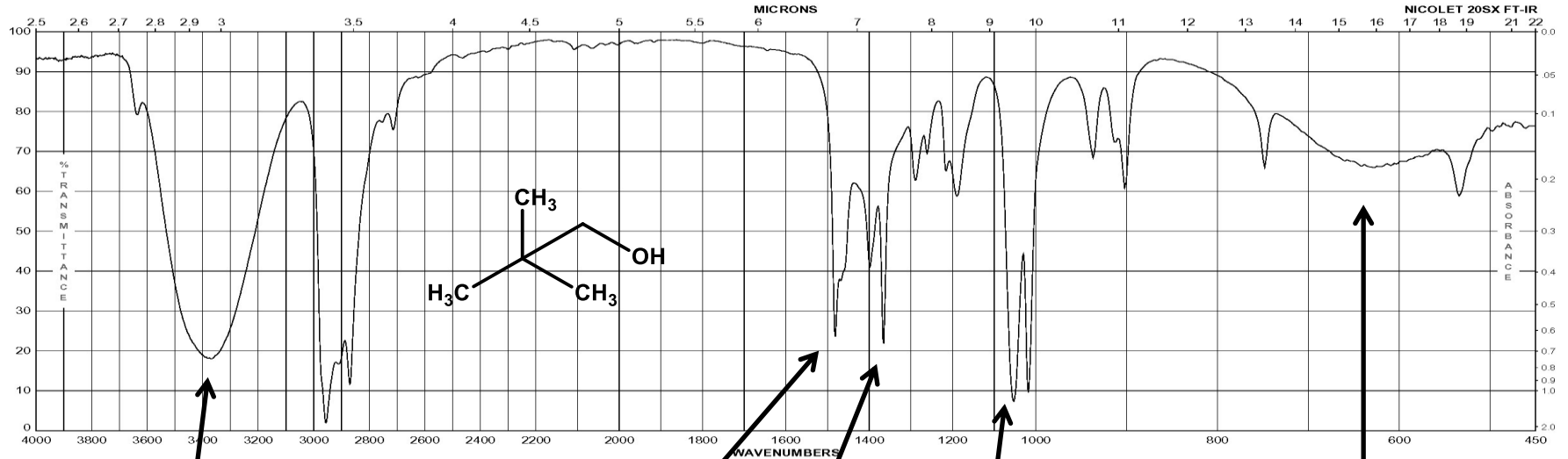
Alcoholic C-O Stretch

	Alcohol Type	Absorption Range cm ⁻¹
1	Saturated tertiary Secondary (highly symmetrical)	1205-1124
3	Secondary saturated, α -unsaturated or cyclic tertiary	1124-1087
4	Secondary α -unsaturated, Secondary alicyclic five or six- membered ring, Saturated primary	1085-1050
5	Tertiary, highly α -unsaturated Secondary di- α -unsaturated Secondary α -unsaturated Secondary alicyclic seven or eight membered ring Primary α -unsaturated	<1050

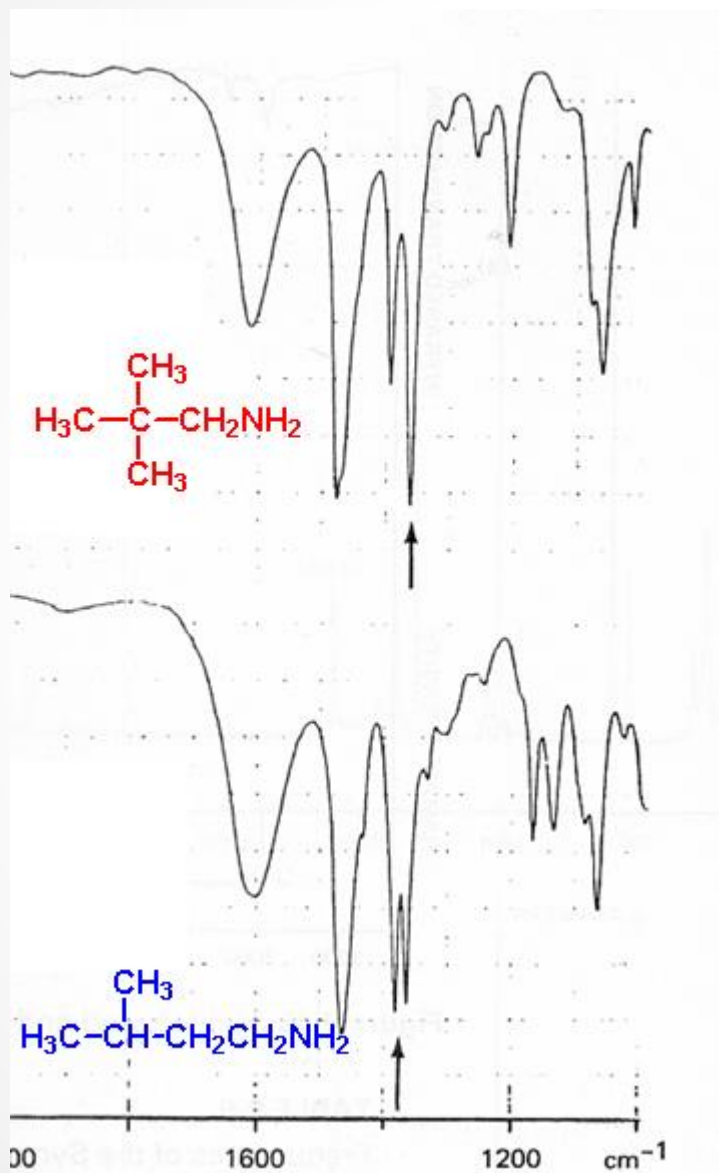
Alcoholic C-O Stretch



Alkyls - Tert-butyl *ver* isopropyl



Tert-butyl *ver* isopropyl

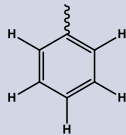
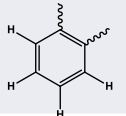
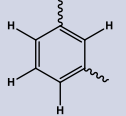
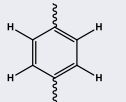
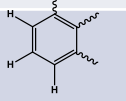
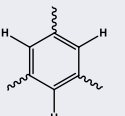


$\delta_s \text{CH}_3$ 1395 and 1370 cm^{-1}

$\delta_s \text{CH}_3$ 1385 and 1370 cm^{-1}

Aromatic Ring Substitution

orto- meta- para-

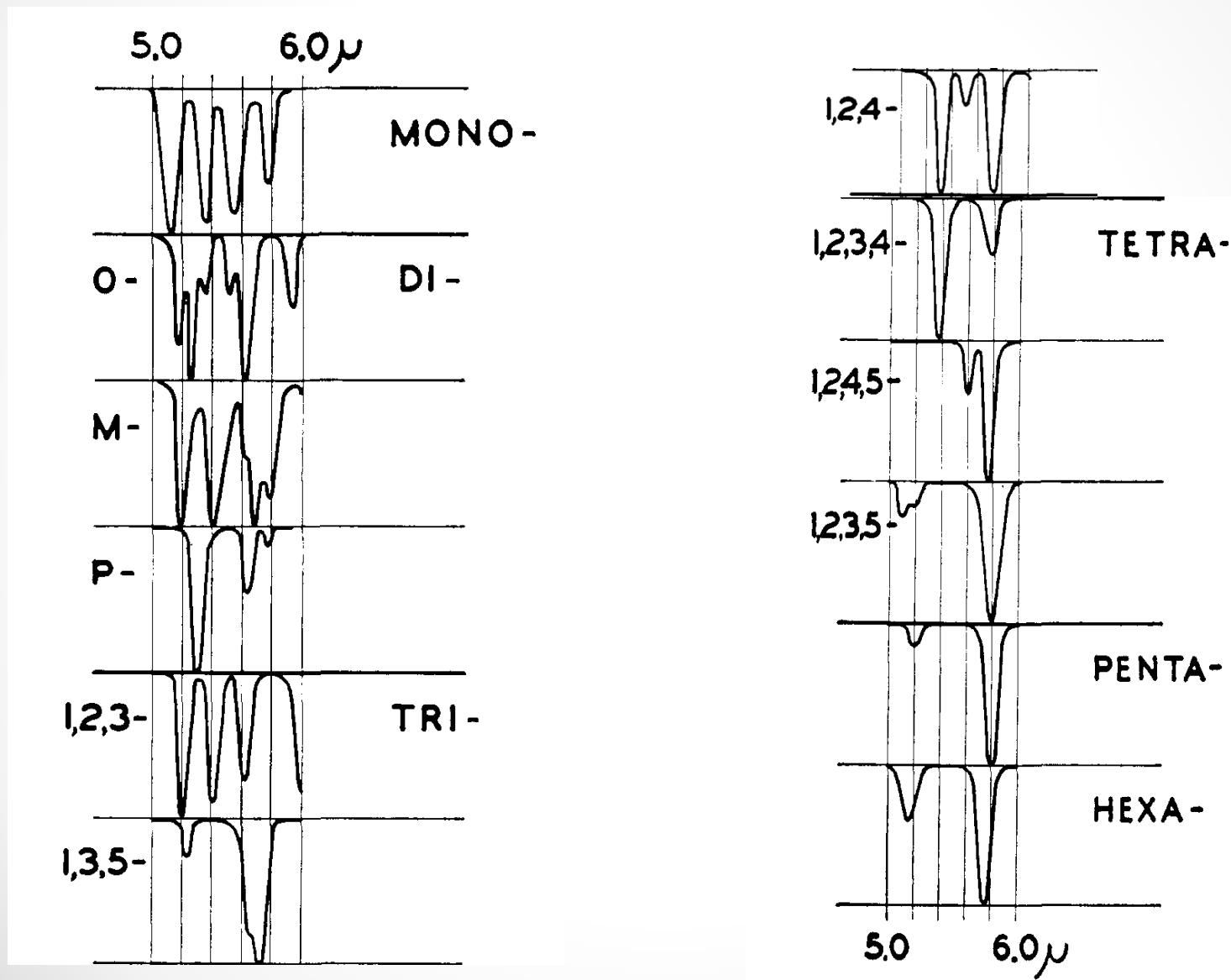
	Substitution	Structure	Range cm^{-1}	Intensity
1	mono		910-890 770-730 710-680	m^* s s
2	1,2-di <i>Ortho-</i>		780-735	s
3	1,3-di <i>meta-</i>		900-835 810-750 725-670	m s m-s
4	1,4-di <i>para-</i> 1,2,3,4-tetra		860-800 860-780	s s
5	1,2,3-tri		800-750 780-760 720-680	s m^* m
6	1,3,5-tri (1,2,3,5-tetra 1,2,4,5-tetra penta-)		900-840 865-800 730-675 900-840	m s m^* m

* Sometimes lack of band

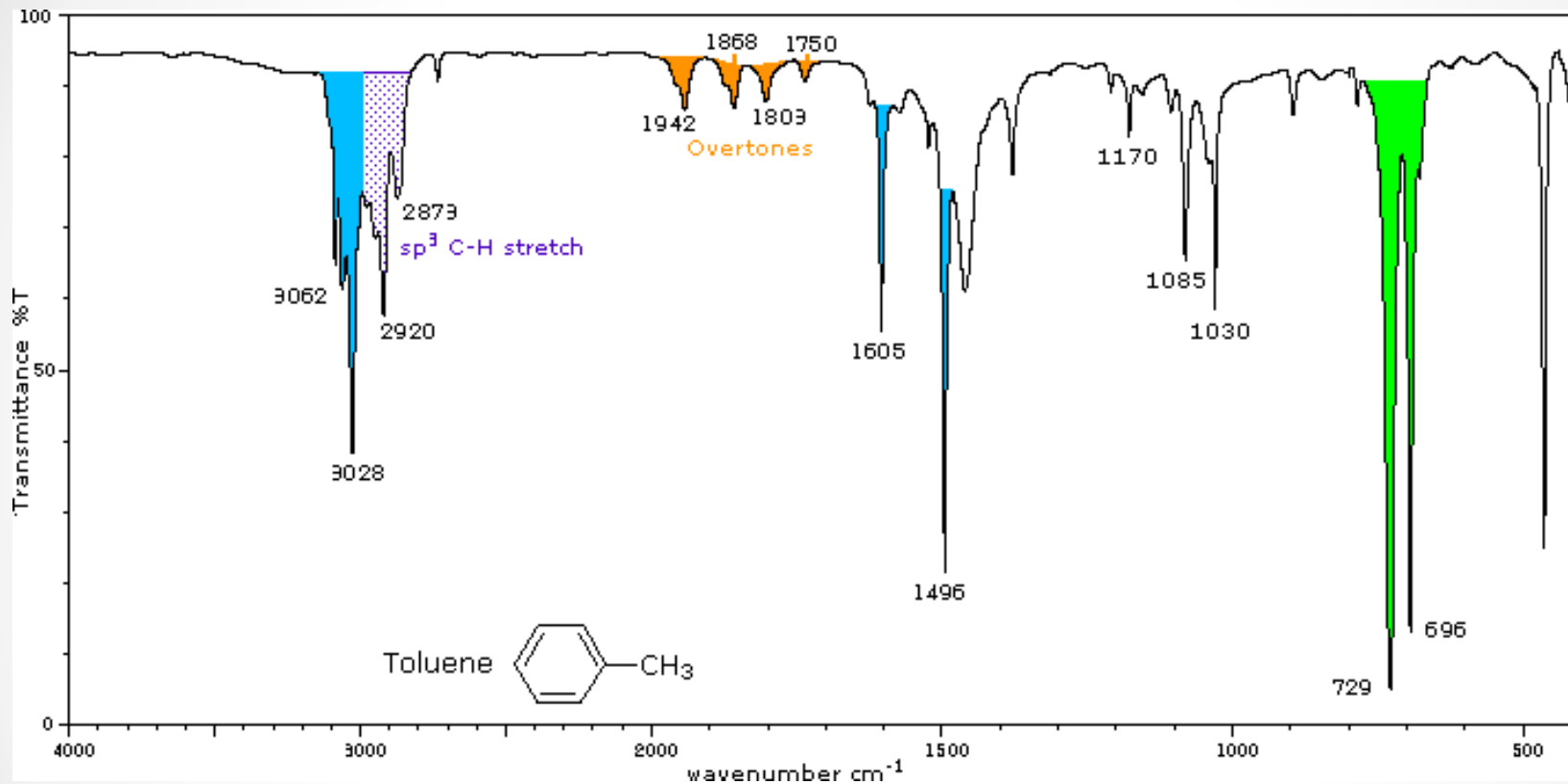
Aromatic Ring Substitution- overtones of γ – out of plane vibration

2000 cm^{-1}

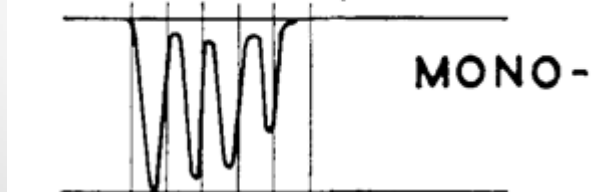
1667 cm^{-1}



Mono substituted

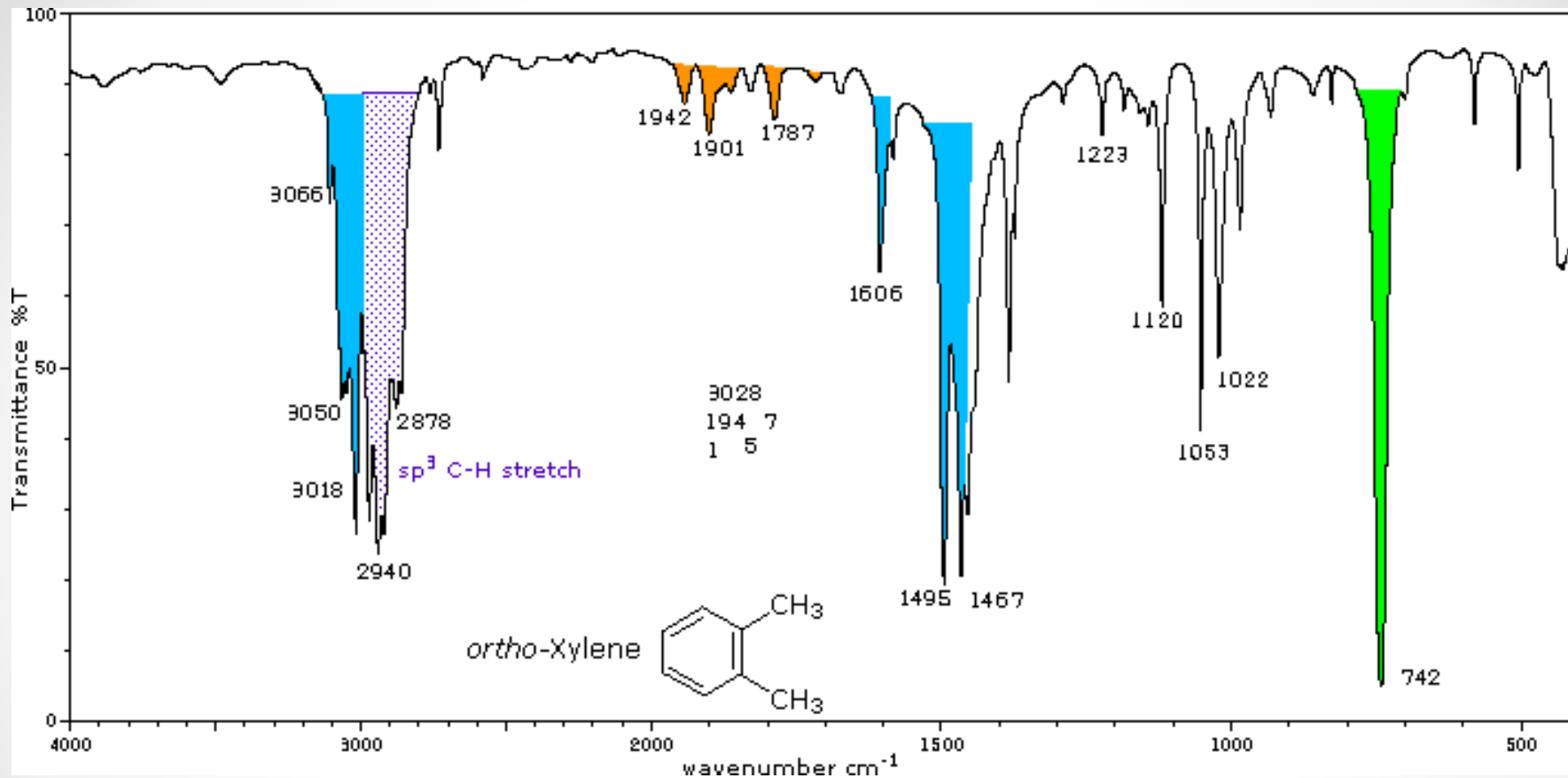


2000 cm^{-1} 5.0 μ 6.0 μ 1667 cm^{-1}



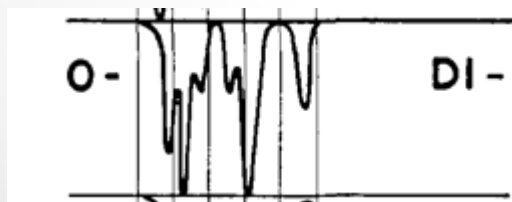
910-890	m^*
770-730	s
710-680	s

Ortho substituted



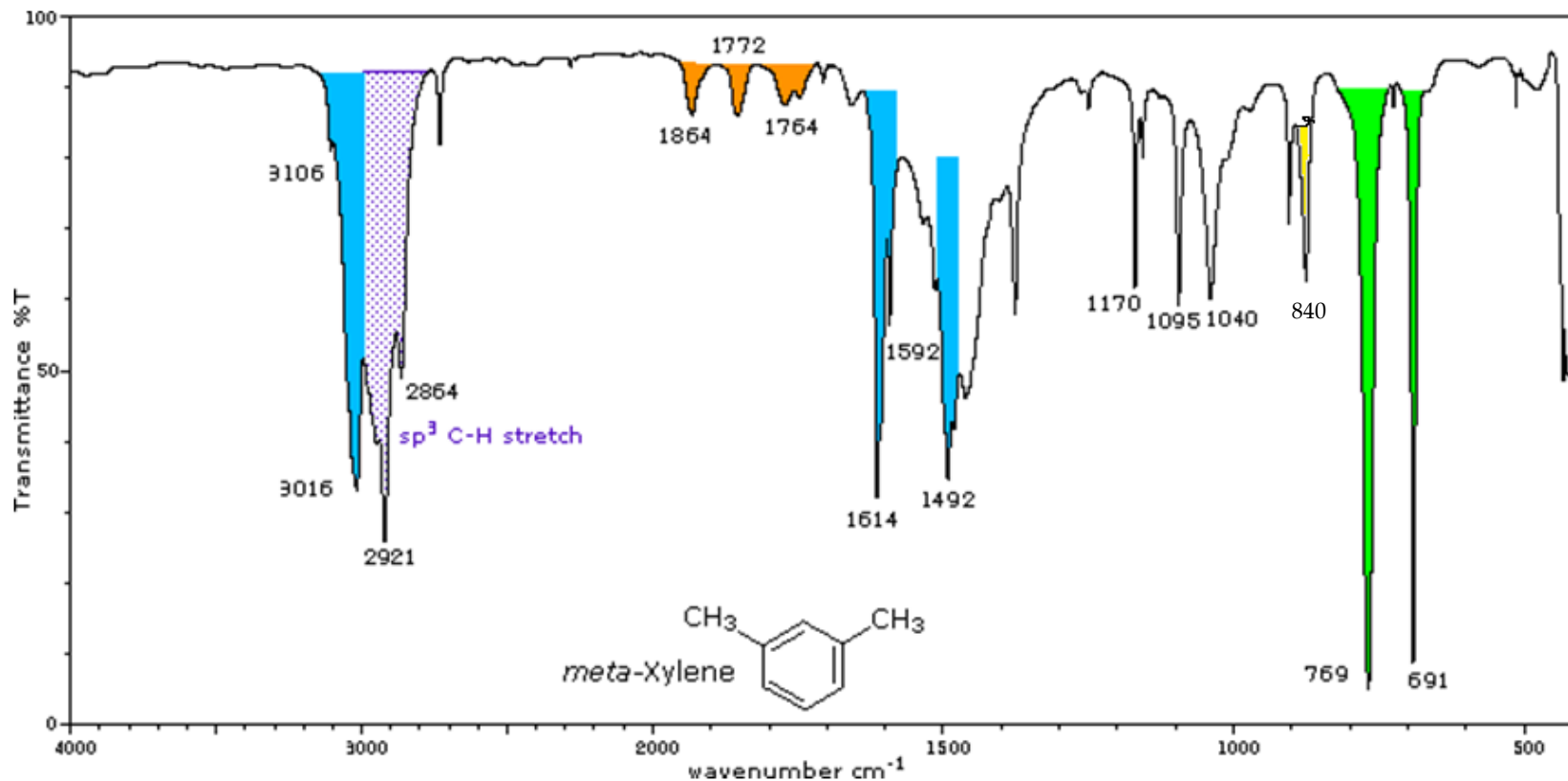
2000 cm^{-1}

1667 cm^{-1}



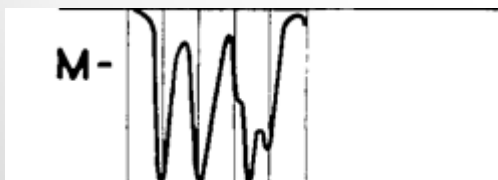
780-735 s

meta substituted



2000 cm^{-1}

1667 cm^{-1}



900-835

m

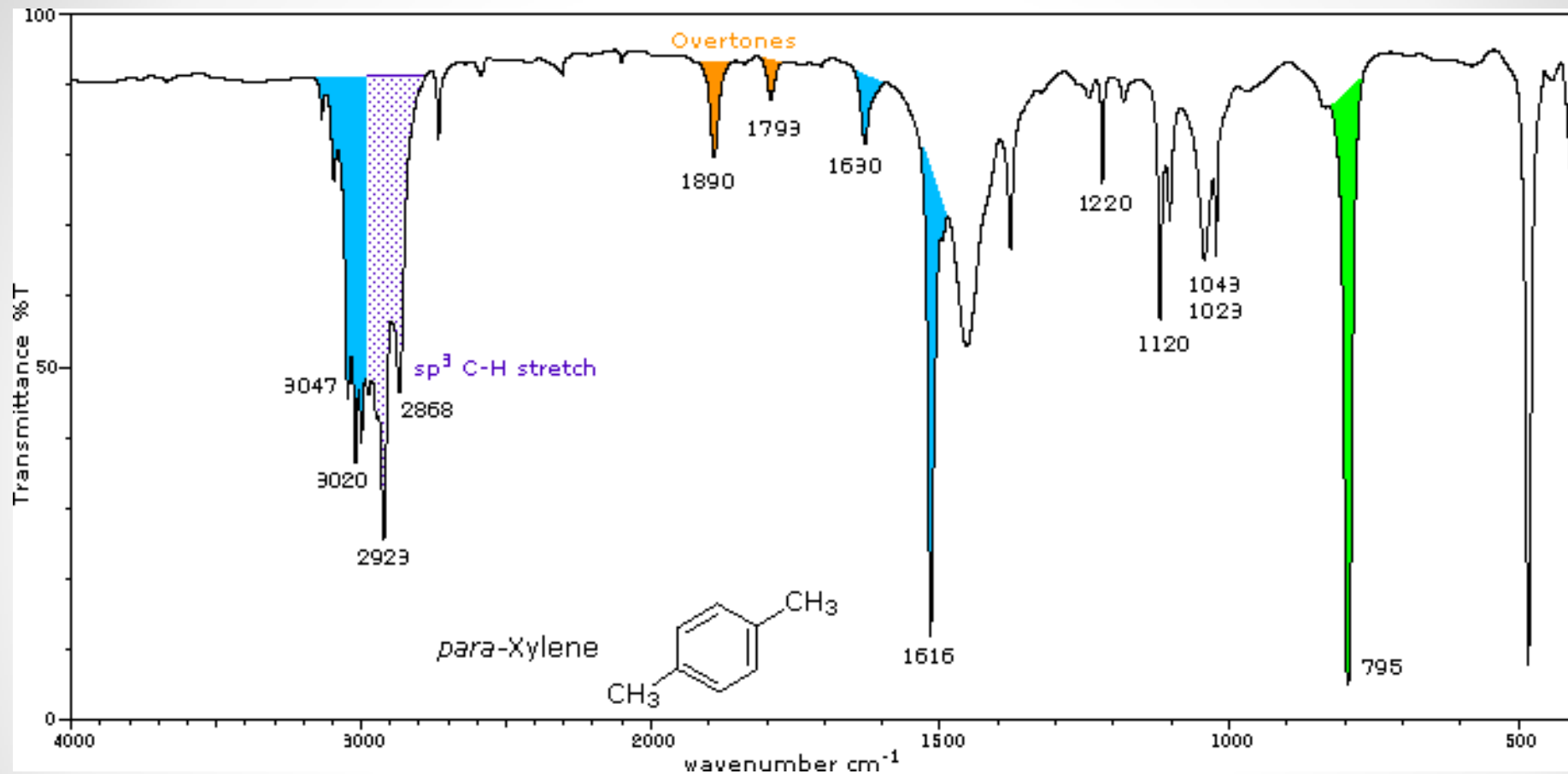
810-750

s

725-670

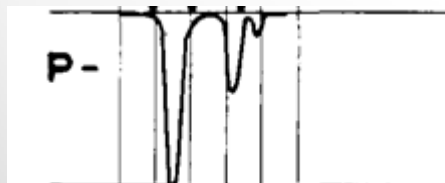
m-s

para substituted



2000 cm^{-1}

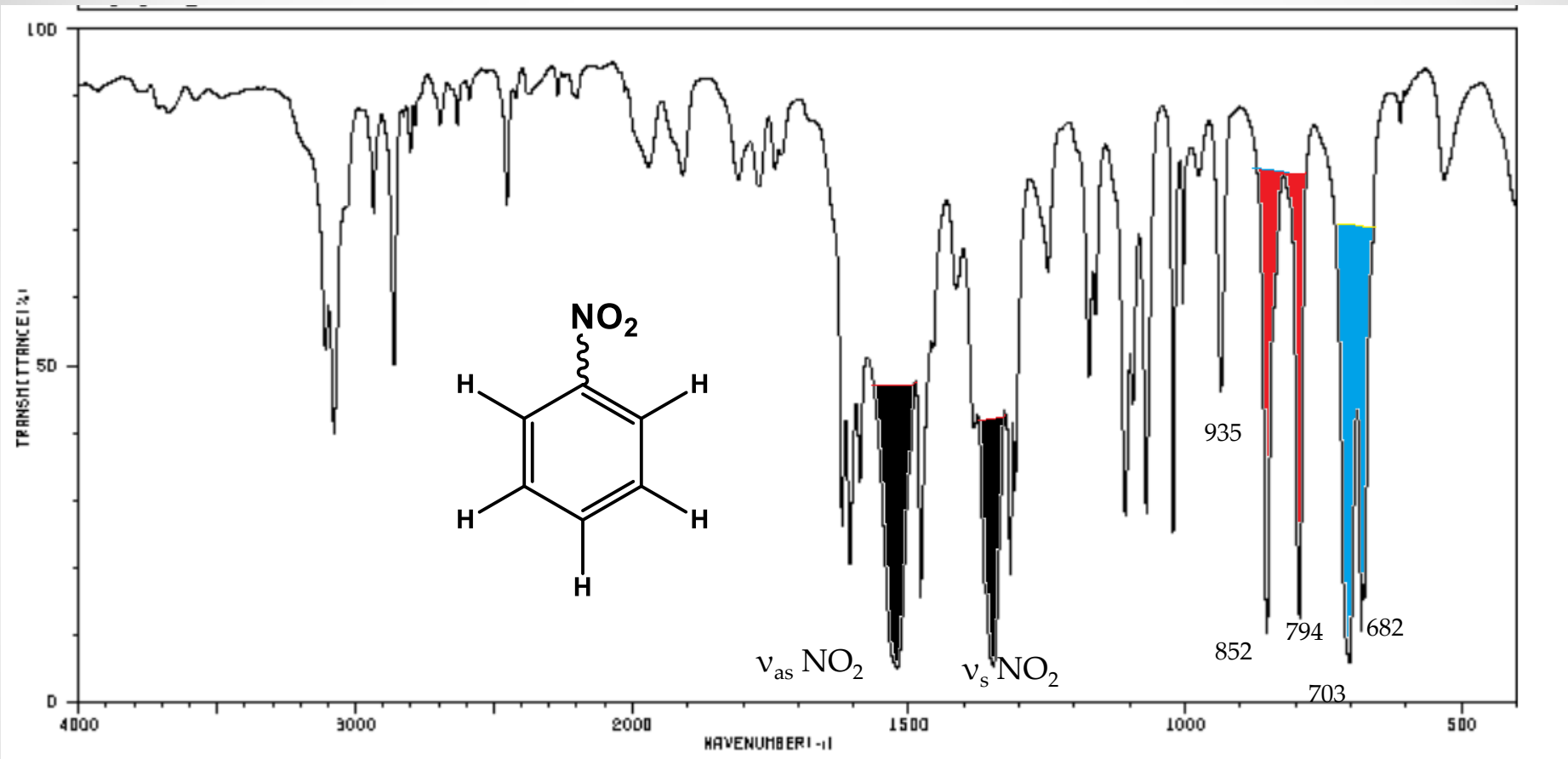
1667 cm^{-1}



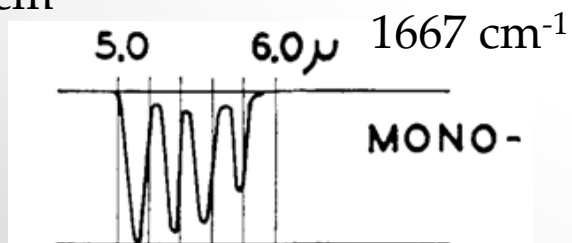
860-800

s

EWG substituted aromatic ring



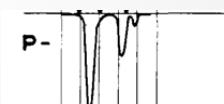
2000 cm⁻¹



mono-

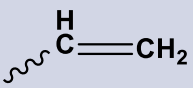
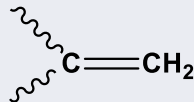
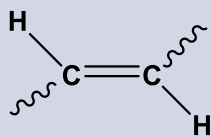
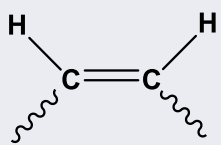
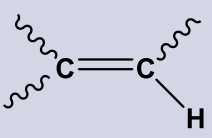
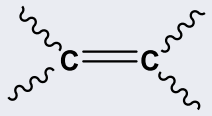
910-890	m*
770-730	s
710-680	s

para- ?

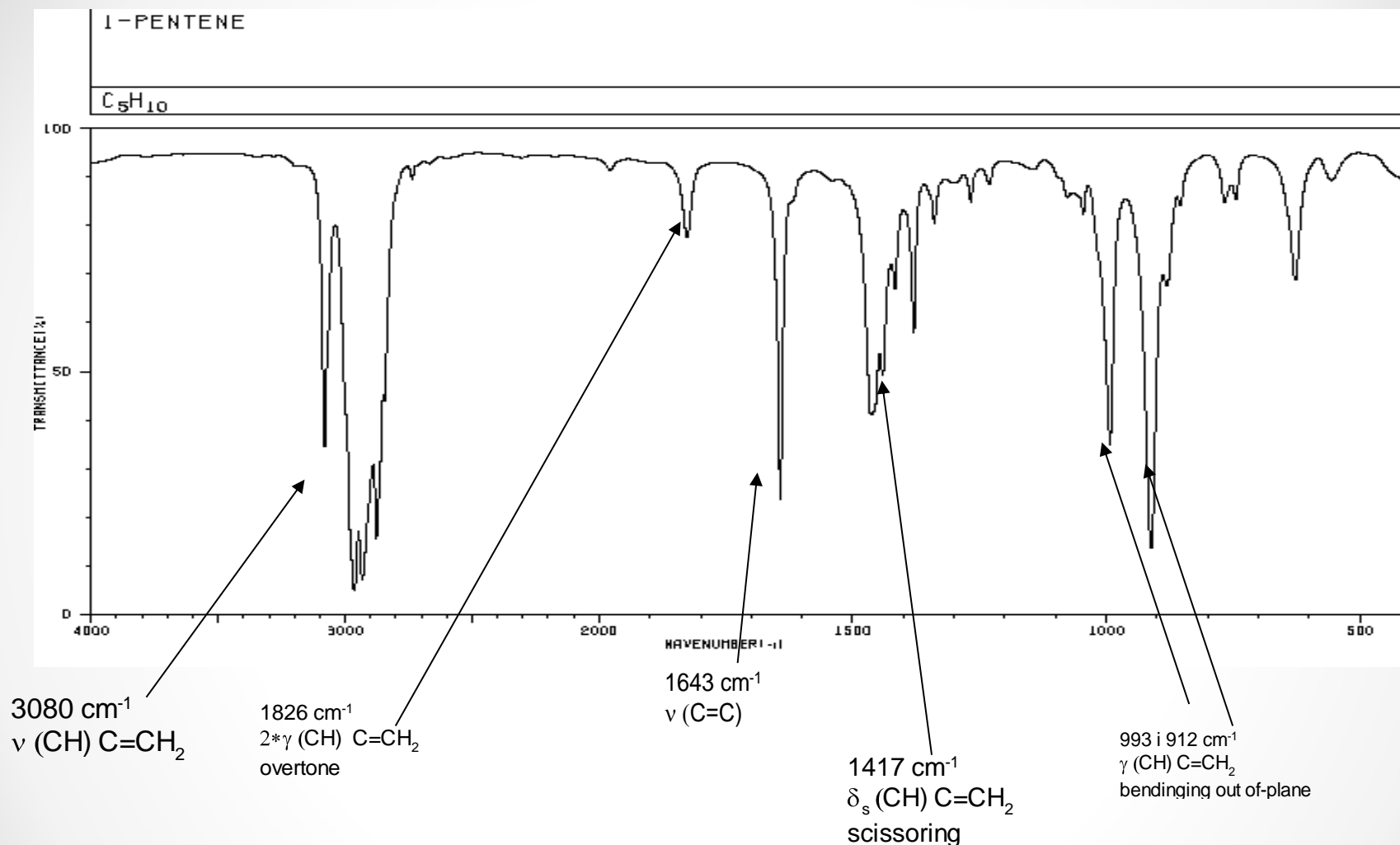


860-800	s
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Alkenes substitution

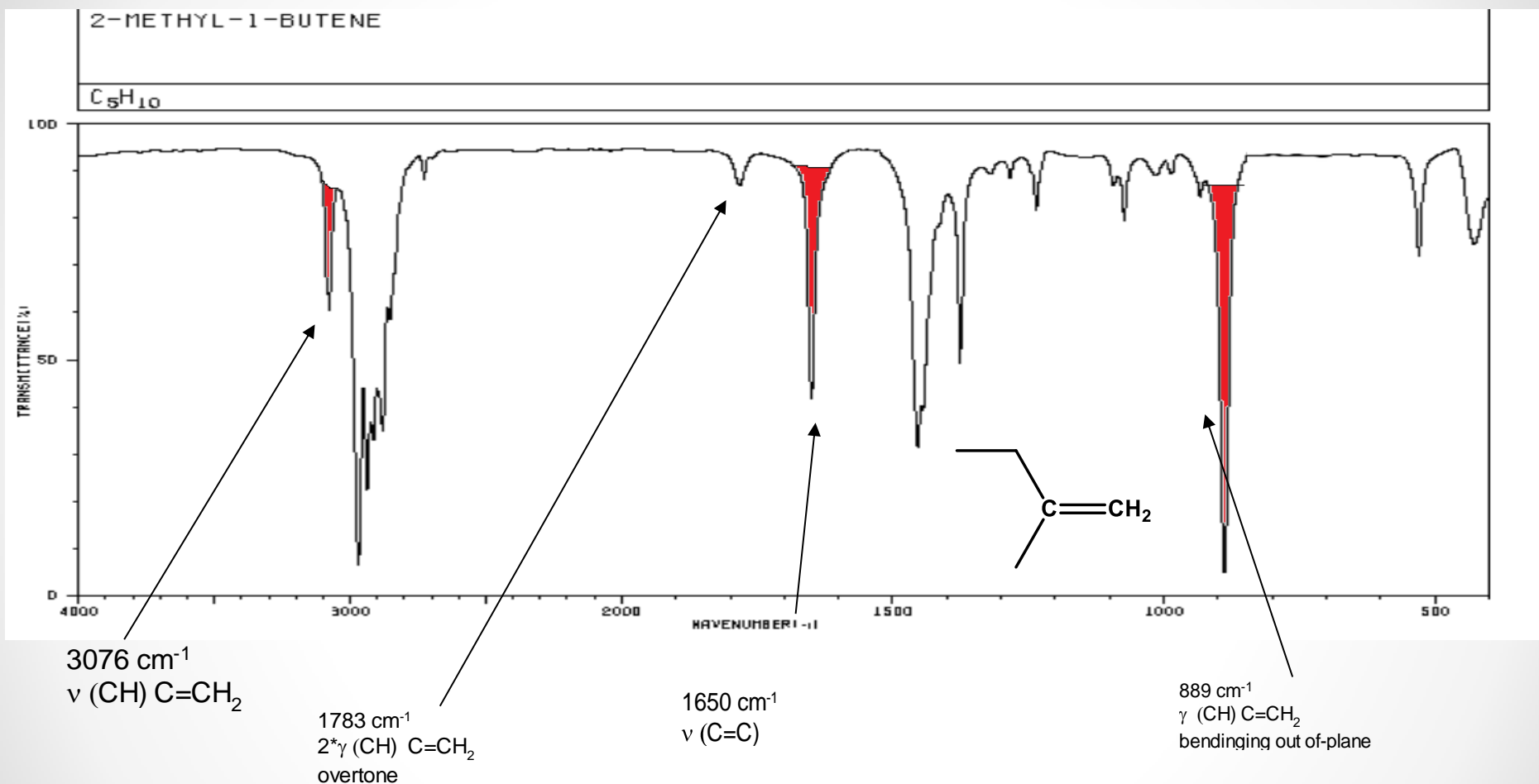
	Structure	(γ) bending out of plane [cm^{-1}]	(ν) stretching =C-H [cm^{-1}]	(ν) stretching C=C [cm^{-1}]	overtones
1		1005-985 s 920-900 s	3095-3075 m 3040-3010 m	1660-1635 m	1860-1800 m
2		900-880 s	3095-3075 m	1660-1640 m	1800-1750 m
3		990-960 s	3040-3010 m	1690-1665 w	-----
4		730-665 m	3040-3010 m	1690-1665 w	-----
5		850-790 m	3040-3010 m	1690-1665 w-m (sometimes absent)	-----
6		-----	-----	1690-1650 w (sometimes absent)	-----

Alkenes substitution - terminal CH₂



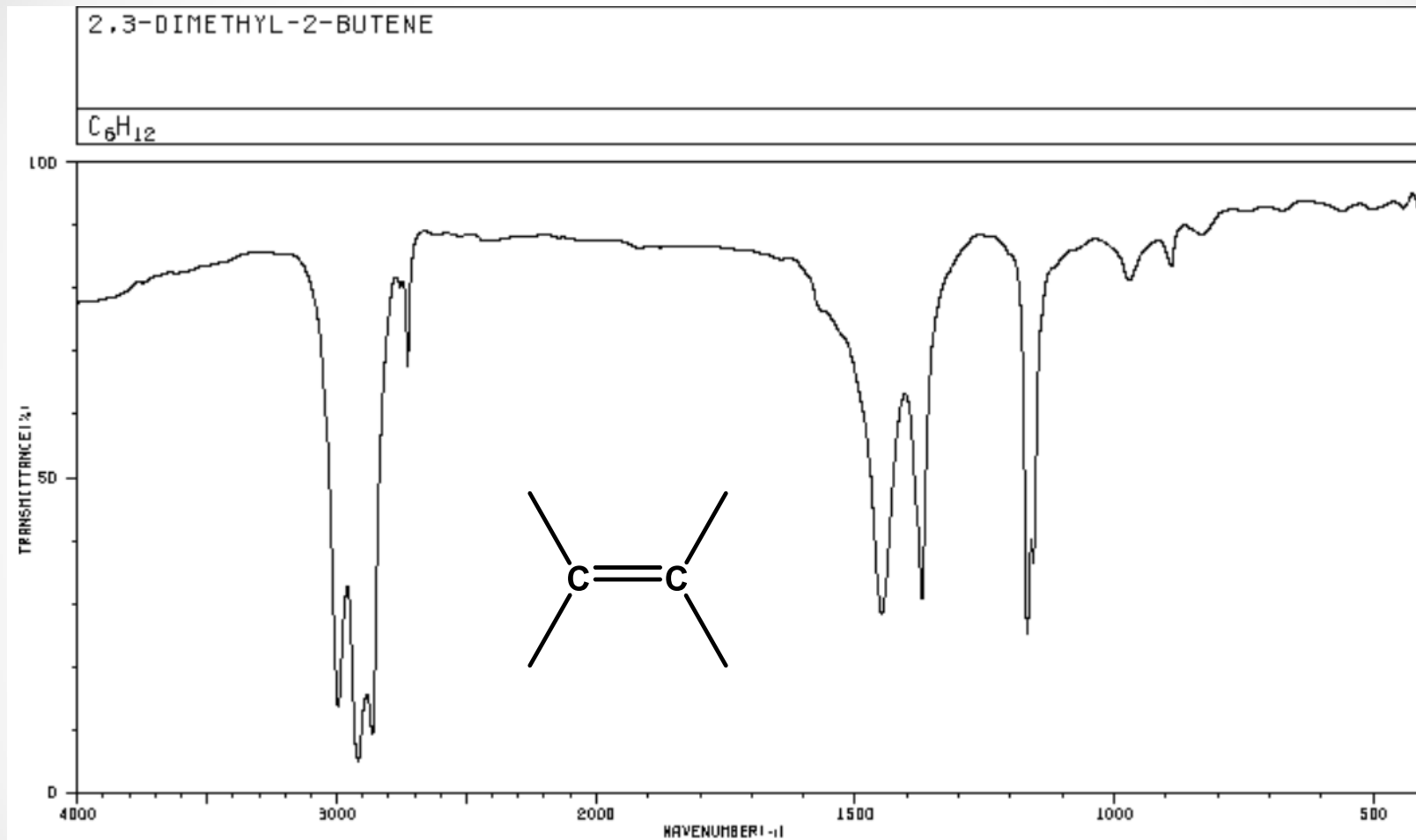
1		1005-985	s	3095-3075	m	1660-1635	m	1860-1800	m
		920-900	s	3040-3010	m				

Alkenes substitution - terminal CH₂



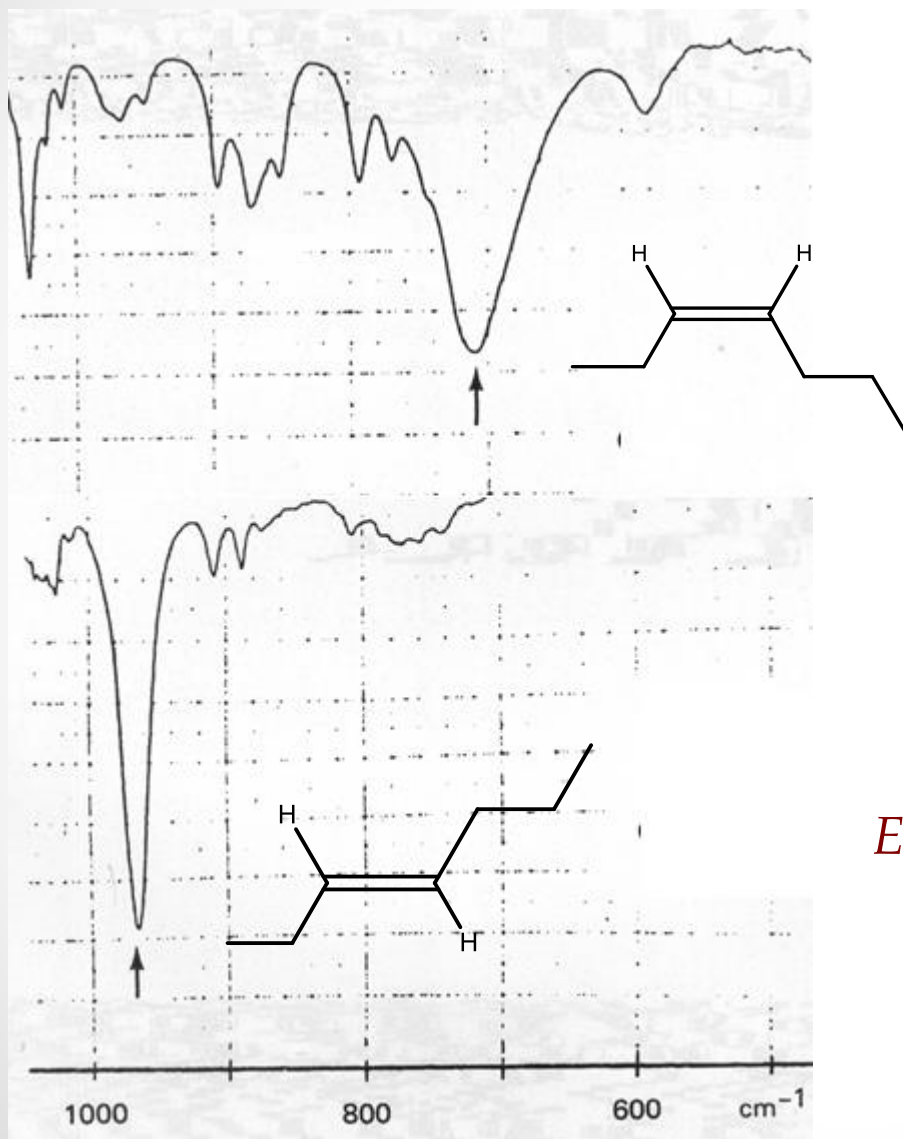
2		900-880	s	3095-3075	m	1660-1640	m	1800-1750	m
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Alkenes substitution



	Structure	(γ) bending out of plane [cm^{-1}]	(ν) stretching =C-H [cm^{-1}]	(ν) stretching C=C [cm^{-1}]	overtones
6		-----	-----	1690-1650 w (sometimes absent)	-----

Alkenes substitution: Z and E



Z γ (C-H) 730 – 665 cm⁻¹
medium intensity

E γ (C-H) 990 – 960 cm⁻¹

Strong intensity